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EXPLORATORY DEVELOPMENT OF ADDITION CURED POLYIMIDE RESINS

*HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA 90230*

AUGUST 1977

TECHNICAL REPORT AFML-TR-72-149
Final Report for Period 1 March 1976 to 30 June 1977

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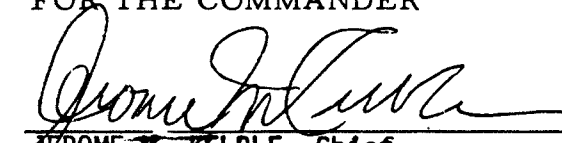
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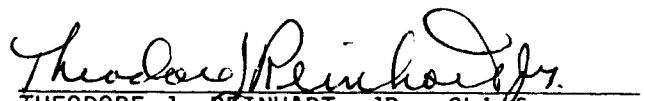
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FOR THE COMMANDER


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Polymer	Adhesive									
Addition Reaction	Weld-Bond									
Polyimide Resin	Reactive Diluent									
Laminating Resin	Tack and Drape									
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Four diethynyl substituted polyimide prepolymers containing, as part of the anhydride moiety, the perfluoroisopropylidene group, were evaluated as reactive diluents for Thermid 600. The desired effects of utilization of these materials were: (1) lowering of cure and postcure temperatures, (2) increasing the liquid temperature range between melt and cure, (3) impart tack and drape qualities to glass and graphite prepregs. The diluents all had lower melting temperatures and cure temperatures than Thermid, and formed homogeneous melt phases with it. Mixtures having the composition of Thermid/										

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diluent equal to 2:1 all had lower melting points than Thermid alone. Laminates were made, and tack and drape properties could be imparted to preregs either by wetting with easily removable solvents, such as acetone, or by heating to melt the prepolymer.

Mixtures of Thermid and diluent were used to prepare weldbond samples. Spotwelding was successful with aluminum filled mixtures of Thermid and diluent in the melt phase. S/N tests were run on spotwelded, adhesive bonded and weldbonded titanium specimens.

The data base for HR602 bonded titanium specimens was expanded to include prepolymer prepared by the NMP solvent process.

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FOREWORD

This technical report was prepared by Hughes Aircraft Company, Aerospace Group, Culver City, California, under U.S. Air Force Contract F33615-76-C-5171. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," and Task No. 03A9, "Structural Plastics and Composites." The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. T. J. Aponyi (AFML/MBC) as the Project Engineer.

This report covers the work performed from 1 March 1976 to 30 June 1977 and is submitted in partial fulfillment of the contract.

The work was performed in the Advanced Technology Laboratory under the management of Mr. L. Brian Keller. The program manager was Dr. Robert H. Boschan. The principal investigator was Dr. Abraham L. Landis. Professional assistance was provided by Dr. Norman Bilow, Senior Scientist, Dr. Daniel A. Demeo, Dr. Thomas W. Giants and Mr. Albert M. Schwider. Professional consultation was provided by Mr. L. Brian Keller, Mr. Arnold J. Tuckerman, Dr. Richard I. Akawie. Research assistance of a very high caliber was provided by Mr. Thomas J. Shudic and Mr. Jeff D. Lohoff. Prepreg and laminate formulation was performed under the direction of Mr. Arturo A. Castillo, assisted by Mr. Clark Staito.

This report was submitted by the authors in July 1977.

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I. INTRODUCTION

Since 1971, Hughes Aircraft Company has, under Air Force Materials Laboratory Contracts, been engaged in the development of high temperature capability prepolymers which cure thermally by addition polymerization processes with no evolution of volatiles. These materials include the acetylene modified polyimides, or HR600 series of oligomers. As part of this work, new monomeric intermediates not previously available were synthesized. Monomer syntheses developed in the course of this study have included 1,3-bis-(m-aminophenoxy)benzene, m-aminophenylacetylene and 3-(3-aminophenoxy)phenylacetylene.

Major applications of the HR600 family of resins have included glass and graphite reinforced composites, adhesives for titanium, and self-lubricating composites. Extensive flexural strength and modulus data of composites, lap shear strengths of adhesive formulations, and friction and wear data of self-lubricating composites, both at ambient and elevated temperatures, and after aging under conditions of high temperature and high humidity, have been compiled as a result of work supported by Air Force contracts as well as Hughes Independent Research and Development Programs.

Other applications of HR600 type resins which have been examined at Hughes to a somewhat lesser degree include adhesive weldbonding, reinforced molding compounds, and copper clad printed wiring boards.

The physical and mechanical property data obtained over a period of several years indicate that the HR600 resins are extremely good. In June 1977, a licensing and marketing agreement was negotiated with the Gulf Chemicals Division of Gulf Oil Company. Currently, Gulf is marketing HR600 under the Gulf Trade name "THERMID 600".

Although the HR600 resins are promising, certain drawbacks were apparent. (1) The required cure temperature (485°F) and postcure temperatures (600° to 700°F) are higher than desired, and the liquid temperature range between the liquid melt and cure should be greater in order to allow for better flow during processing. (2) Prepregs resulting from impregnation of glass or graphite reinforcements with HR600 are dry and somewhat boardy, and do not possess tack, which makes laying up plies difficult.

It is thus the objective of this program to accomplish: (1) lowering of cure and postcure temperatures; (2) increasing the liquid temperature range between melt and cure; (3) improving the tack and drape qualities of prepregs; and (4) expand the data base for reinforced composites and adhesive bonded joints.

II. SUMMARY

The approach to the improvement of tack and drape of glass and graphite HR600 composites in the current program has been to find reactive diluents which become an integral part of the polymeric network and do not act as inert volatile materials which boil off during cure. The diluents studied were diacetylene substituted prepolymers which could copolymerize with the HR600 oligomer to yield thermally stable polymers. In order to improve processability, materials were sought which have lower melting points than HR600 so that a broader range exists between melt and cure temperatures. Several such materials were examined. The reactive diluents chosen for further study were derived from two anhydrides containing the hexafluoroisopropylidene group. These anhydrides were (1) 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride, which is proprietary to duPont and designated as 6F, and (2) 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl] hexafluoropropane dianhydride, which is proprietary to TRW and designated BFDA. Four monomers were prepared from these anhydrides utilizing, in addition to the anhydrides, aminophenylacetylene (APA) and 1,3-bis(3-aminophenoxy) benzene (BAPB).

Physical and chemical properties of these four neat diluents, in addition to cure and molding parameters and physical and mechanical properties of glass and graphite laminates made from these materials, were studied as part of Hughes Internal Research and Development Programs.

In the current AFML sponsored program, mixtures of HR600 (Gulf THERMID 600) with each of the above reactive diluents in the ratio 2 parts THERMID 600: 1 part reactive diluent by weight have been studied. All of these mixtures had lower melting temperatures than THERMID 600 and, in one case, the mixture melted more than 100°C below the melting temperature

of THERMID 600. After determination of physical, chemical and thermal properties of these mixtures, glass and graphite reinforced composites were studied.

Weight loss data on a glass laminate (7781/CS290) made from one of the reactive diluents studied, APA-6F-BAPB-6F-APA, indicated superior thermal stability over that observed for THERMID 600 at 600°F for 1000 hours. After 1000 hours at 600°F, the laminate prepared from neat reactive diluent lost 5.2 percent, the laminate from a mixture of two parts THERMID 600: one part diluent lost 18.6 percent, and the laminate from THERMID 600 lost 27.7 percent.

A Thornel 300 unidirectional graphite laminate made from the above 2:1 mixture had ambient and 600° flexural strength and modulus comparable to that observed for a similar laminate made with THERMID 600. Thirty day humidity aging tests at 80°C and 95 percent RH on these graphite laminates showed excellent retention of ambient and elevated temperature strength and modulus properties for both THERMID 600 and the 2:1 THERMID 600: reactive diluent mixture.

Better retention of mechanical properties and lower weight loss upon 600°F long term exposure are expected after further optimization of postcure cycles and possibly upon substitution of more highly pyrolyzed graphite such as HTS or GY-70.

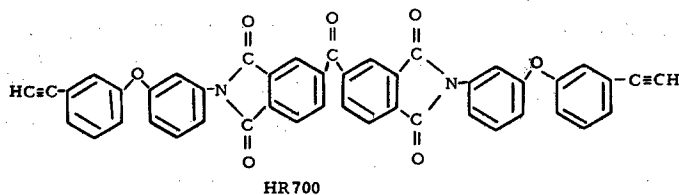
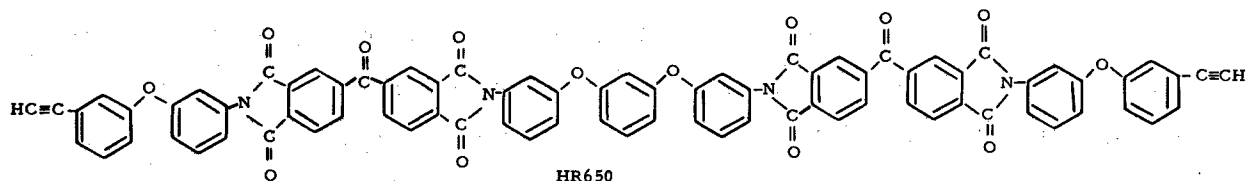
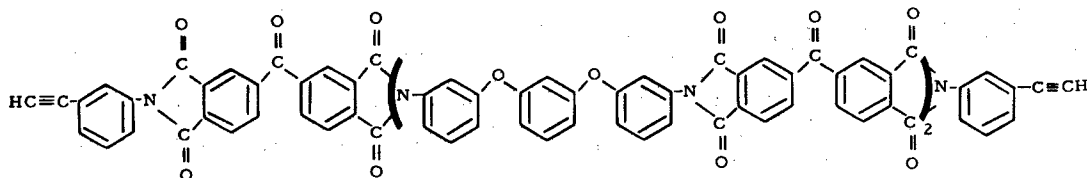
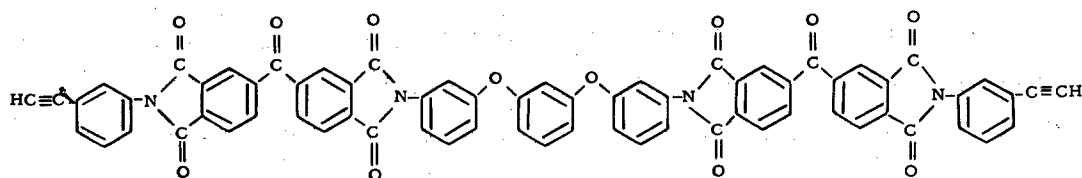
In the adhesive portion of this study, HR602 (formerly HR600 DP-2) was prepared by the modified Gulf process, which eliminates the use of two solvents previously used, namely m-cresol and dimethylformamide. Lap shear strength tests with and without aluminum filler were completed, and optimization studies of prepreg drying and cure cycles were conducted.

The adhesive studies showed that, among several methods of imidization of HR602 that were studied, adhesive prepreg made from a 50:50 mixture of N-methylpyrrolidinone (NMP) imidized and trifluoroacetic anhydride imidized HR602 gave the best and most consistent lap shear strengths, namely 3400-3500 psi at ambient temperature and 1800-2000 at 260°C (500°F).

III. TECHNICAL DISCUSSION

A. ACETYLENE SUBSTITUTED POLYIMIDE OLIGOMERS

As part of previous programs concerned with addition cured polyimide resins, prepolymers including HR600, HR600 DP-2 (now referred to as HR602), HR650, and HR700 were conceived and synthesized. The structures of these prepolymers are shown below.



In the course of these studies, HR600 demonstrated superior properties as a matrix resin in glass and graphite reinforced composites, and as an adhesive for titanium. In addition, the utilization of HR602 and HR650 in titanium bonding was studied, as well as the use of HR700 in graphite reinforced molding compounds. In all cases, the results were extremely encouraging, and the superior performance of thermally cured, acetylene-terminated polyimide oligomer systems was amply demonstrated. During the present study, certain modifications were made on these resins to increase their processability and versatility. These modifications concerned themselves with (1) improvement of tack and drape of oligomer impregnated glass and graphite reinforced preregs; (2) lowering of the melting point of the prepolymer; (3) improvement of wetting of titanium adherends for spot welding through metal-filled adhesive formulations in weldbonding; (4) lowering of cure temperature in weldbond formulations. The approach used to reach the first three objectives was to use acetylene-terminated reactive diluents which cure with the acetylene-terminated prepolymers, leaving no voids. The fourth objective was studied by the use of organometallic catalysts which are known to be extremely effective in accelerating acetylenic cyclooligomerization.

1. Reactive Diluent Studies

The two major problems to be resolved in improving the processability of the HR600 type oligomers are to (1) provide sufficient fluidity at a reasonably low temperature to allow good flow of the resin through the reinforcing matrices prior to cure and to compensate for uneven temperature distribution in the processing of large parts and (2) to provide tack and drape characteristics to glass and graphite resin preregs. To solve these problems we have prepared a number of acetylene containing diluents, which are lower melting materials and which form a homogeneous solution at the processing temperature with Thermid 600 oligomer. These diluents were chosen so that the thermal stability or physical and mechanical properties of molded parts would not be seriously compromised. To meet these requirements, diluents were chosen such that the molecular backbone would include some imide, amide or ether linkages. Reactive diluents containing these

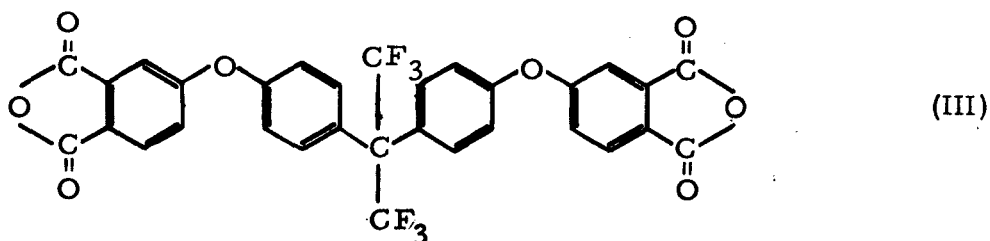
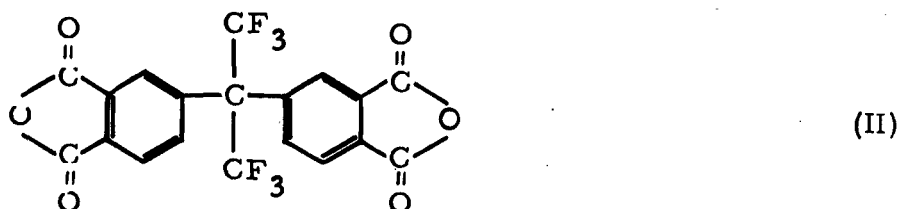
groups would be likely to form lower melting homogeneous solutions with the HR600. Since the homopolymerization reaction is temperature dependent, lower molding temperatures would therefore result in longer gel times and therefore improve processability. Thus, the main purpose of introducing a reactive diluent would be to increase the fluidity range, i. e., the range between the melting temperature and the cure temperature of the oligomer. This extension of liquid range prior to cure is likewise important in imparting tack and drape characteristics to a glass or graphite prepreg prepared from an oligomeric mixture.

We have succeeded in preparing a number of promising candidate reactive diluents. The most successful diluents were prepared from acid dianhydrides containing the perfluoroisopropylidene group (I). These diluents came about as a result of Hughes Aircraft Co. Independent Research and Development. The utility of these diluents to help accomplish the goals of the present program became apparent after examining their physical and chemical properties. This molecular moiety, when present as part of an oligomer backbone, improves tractability and fluidity when compared to such groups as carbonyl, sulfur, methylene or oxygen. Thus, the substitution of the hexafluoroisopropylidene group for the carbonyl group in polyimide type prepolymers yielded materials which are more soluble and have lower melting temperatures. Also, the cured polymers have good oxidative stability.⁽¹⁾

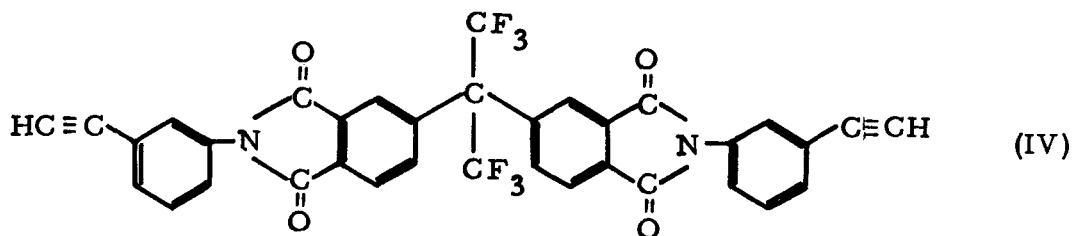


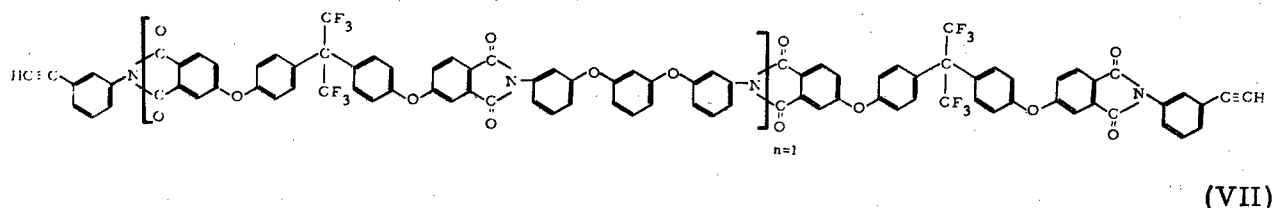
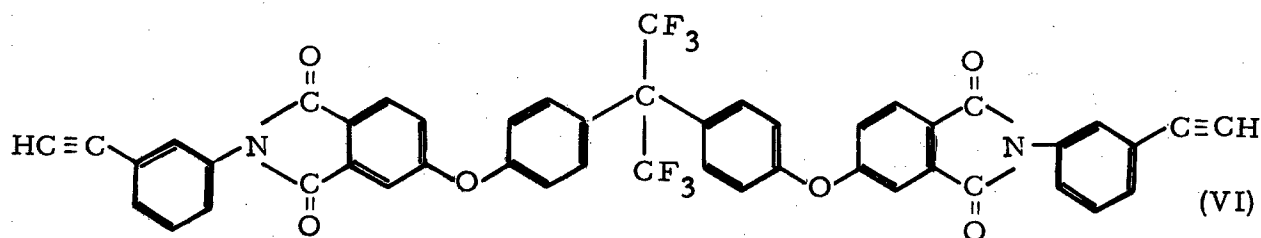
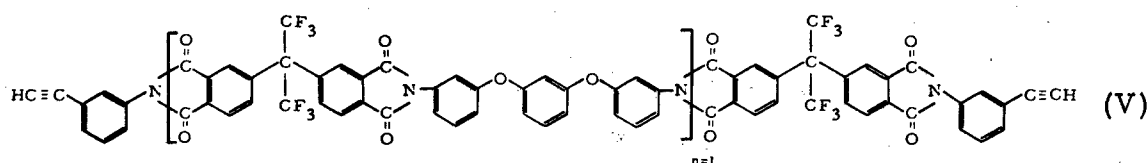
¹H. H. Gibbs, and C. V. Breder, Polymer Preprints (April 1974 ACS) Vol. 15, No. 1, pp 775-780.

To prepare these diluents we have utilized two acid dianhydrides containing the perfluoroisopropylidene moiety. These are 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (II) made by E. I. DuPont de Nemours and Company, and incorporated into various polyimides and the analogous compound, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane dianhydride (III) first prepared by Drs. Robert Jones and Michael O'Rell of TRW, Inc.



Compound II is known as 6F by DuPont and III as BFDA by TRW. Four diluents were prepared from these intermediates by reaction with and without 1, 3-bis (3-aminophenoxy)benzene and 3-aminophenylacetylene. The structures are shown below.





For ease in identifying these materials, the structures IV, V, VI and VII will be symbolized according to the reactants used in their preparation. Thus, the symbol for 3-aminophenylacetylene will be APA, 1,3-bis(3-aminophenoxy) benzene BAPB, Compound II, 6F, compound III BFDA. Thus, the nomenclature for IV would therefore be APA-6F-APA; V, APA-6F-BAPB-6F-APA; VI, APA-BFDA-APA and VII, APA-BFDA-BAPB-BFDA-APA. The properties for these reactive diluents and mixtures of Thermid 600 are shown in Table I. The differential thermal analysis (DSC) for these mixtures and diluents are shown in Figures 1 through 4. It is interesting to note that these diluent mixtures have melting points lower than that of Thermid 600 and thereby reduce the requisite molding temperature. Furthermore, the diluents are very soluble in acetone. In fact, prepregs made with Thermid 600 and one of these diluents can easily be made tacky by spraying with acetone. The prepregs stick together and the acetone is easily lost by evaporation after tacking the prepregs together. The DSC data show that the exotherm maximum of the mixture is the average of the maximum exotherms of the two constituents.

TABLE I. PROPERTIES OF ACETYLENE-TERMINATED REACTIVE DILUENTS AND
1:2 W/W MIXTURES* WITH THERMID 600

Diluent	Batch No.	M. P. °C	DSC Maximum Exotherm °C	Comments
APA-6F-APA ¹⁾	H2898-46, 57, 76	190 - 194	200	Very soluble in acetone
APA-6F-BAPB-6F-APA	H2898-45, 59, 63	145 - 160	235	Soluble in acetone
APA-BFDA-APA	H2898-55	124	235	Soluble in acetone
APA-BFDA-BAPB-BFDA-APA	H2898-53	160	250	Soluble in acetone
APA-BFDA-BAPB-BFDA-APA/ Thermid 600	H2898-53 Thermid 600	101	250	--
APA-BFDA-APA/Thermid 600	H2898-55 Thermid 600	113	250	--
APA-6F-APA/Thermid 600	H2898-571 Thermid 600	174	240	--
APA-6F-BAPB-6F-APA/ Thermid 600	H2898-59/ Thermid 600	124	250	--

* Blending of 1 part of reactive diluent and 2 parts of Thermid 600 was achieved by ball milling using acetone as suspension medium and then drying at 160°F/4 hours in air circulating oven.

¹⁾ Recrystallized from absolute ethanol.

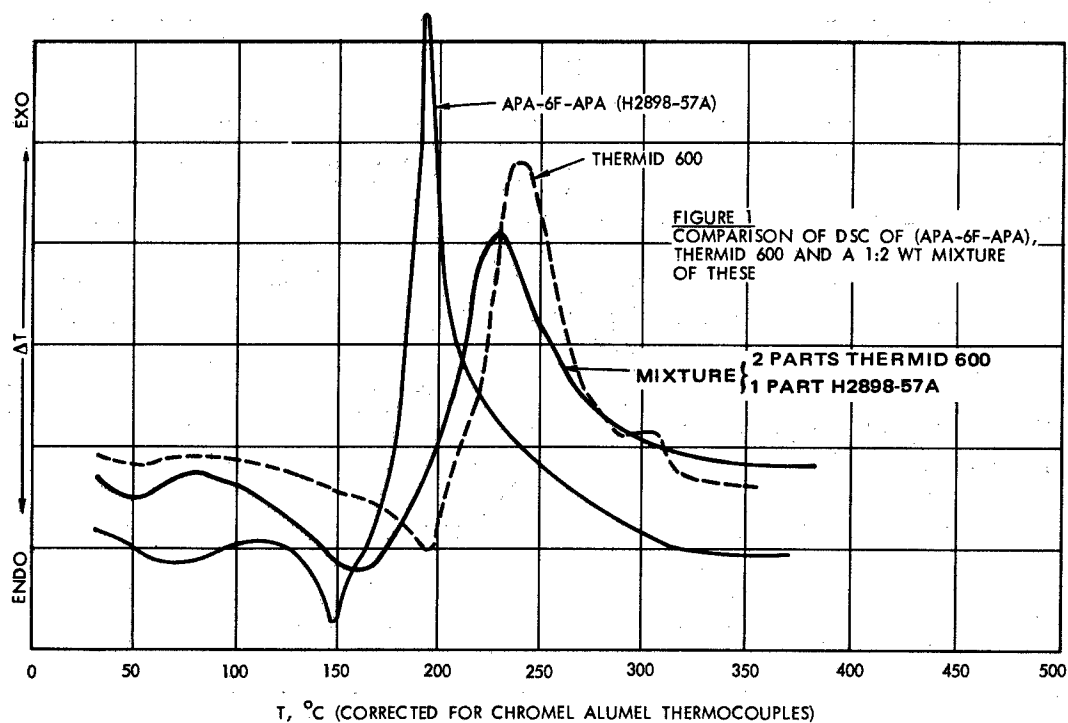


Figure 1. Comparison of DSC of (APA-6F-APA), Thermid 600 and a 1:2 w/w mixture of these.

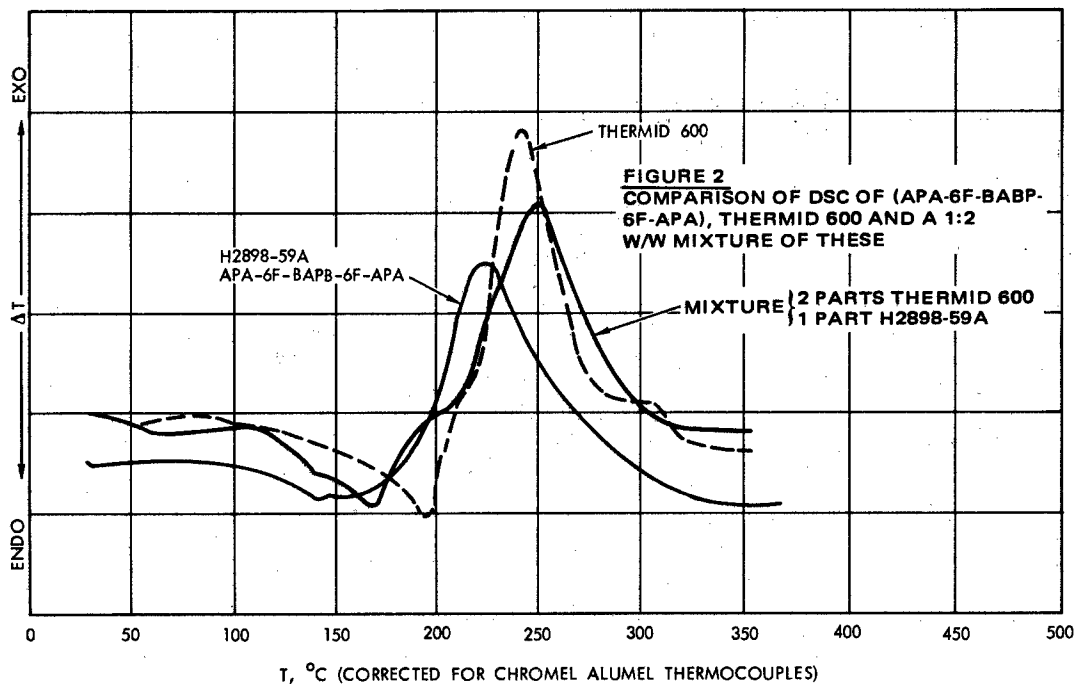


Figure 2. Comparison of DSC of (APA-6F-BAPB-6F-APA), Thermid 600 and a 1:2 w/w mixture of these.

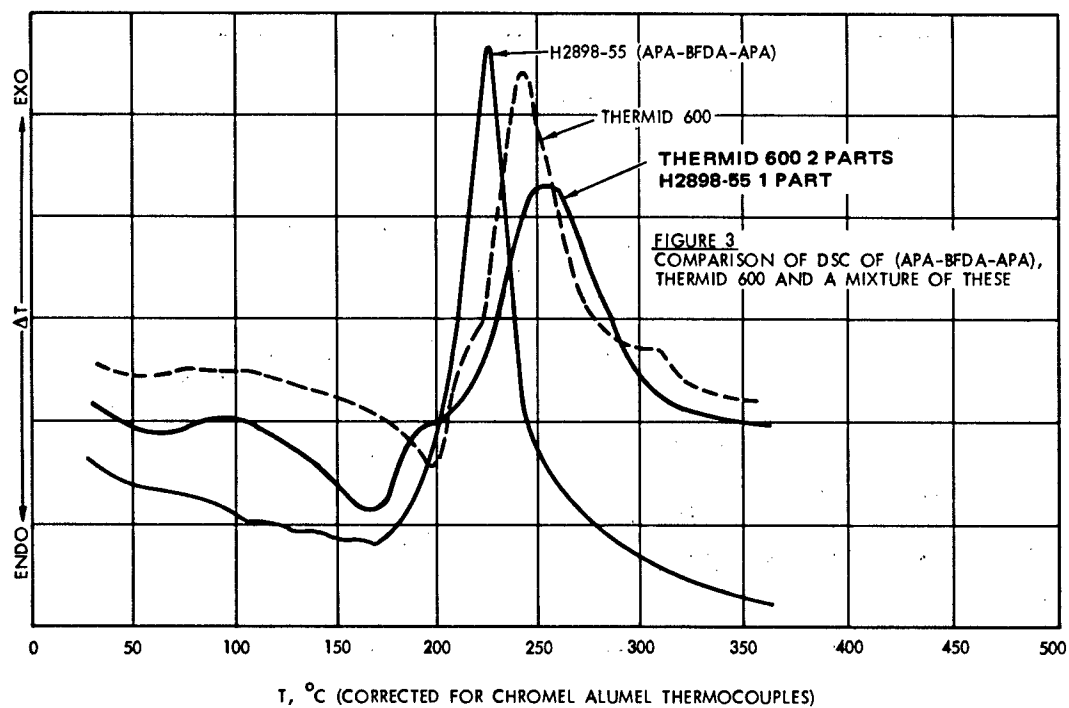


Figure 3. Comparison of DSC of (APA-BFDA-APA), Thermid 600 and a mixture of these.

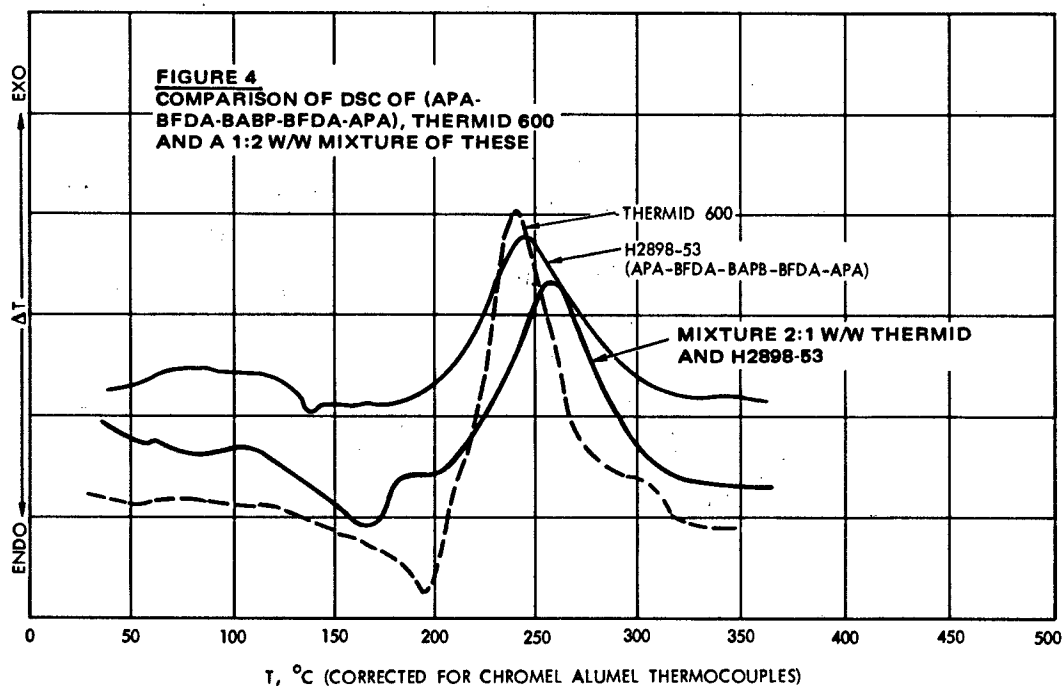


Figure 4. Comparison of DSC of (APA-BFDA-BAPB-BFDA-APA), Thermid 600 and a 1:2 w/w mixture of these.

Neat pellets were molded from these diluents and their mixtures with Thermid 600. The processing data for these mixtures are summarized in Table II. The pellets did not deform upon postcure. Table III summarizes the DSC, TMA data for the neat reactive diluents after postcure.

It can be seen that the onset of the homopolymerization of the diluent is in the same temperature range as that of Thermid 600. For the acetylene-terminated diimide monomers, the onset of the exotherm is lower than for the Thermid because of the higher concentration of acetylenic groups and possibly greater reactivity.

In Table IV, a summary of TGA data for some of the reactive diluents and their mixtures with Thermid 600 is presented. The thermal stability of either of the neat diluents and their mixtures with Thermid 600 is comparable. Thus, the excellent thermal stability of Thermid 600 would not be compromised by formulation with these diluents.

The long term oxidative stability at 600°F (316°C) of the diluents and a mixture of one of these with Thermid 600 is shown in Table V. In the one case in which the mixture is depicted, 2 parts Thermid 600 and 1 part diluent (APA-6F-BAPB-6F-APA), the oxidative stability was much better than the unblended Thermid 600. The oxidative stability of the diluents in general were better than that of Thermid 600.

Thermal mechanical properties were collected on a glass fabric reinforced laminate for the diluent (APA-6F-BAPB-6F-APA) as a function of thermal aging in air at 600°F (316°C). Even after 1450 hours at 600°F, almost 30 percent of the room temperature flexural strength and 57 percent of the 600°F (316°C) strength was retained. The results are shown in Table VI. It should be noted that these values are for an unoptimized process for the preparation of the laminate.

Data were also gathered on long term humidity and elevated temperature exposure for graphite laminates made from Thornel 300 and Thermid 600 made with this diluent. A blend of two parts of Thermid 600 and one part of reactive diluent (APA-6F-BAPB-6F-APA) was used. Thus, two 8 inches by 9 inches by 8 ply, unidirectional panels, were made for both the Thermid 600 (lot 7C902) control and the Thermid 600/reactive diluent mixture.

TABLE II. MOLDING PARAMETERS FOR NEAT PELLETS AND 2:1 W/W MIXTURES OF REACTIVE DILUENTS* AND THERMID 600

Material Description and Batch No. of Diluent	Processing Parameters				Density as Molded gms/cc	Wt Loss After Post Cure** Wt, %	Comments
	Gel Time Seconds	Molding Temp °C	Molding Pressure psi	Cure Time Minutes			
APA-BFDA-BAPB-BFDA-APA (H2898-53)	120	250	1000	120	1.38	3.13	--
APA-BFDA-APA (H2898-55)	160	235	1000	120	1.38	2.62	--
APA-6F-APA (H2898-57)	100	200	1000	120	1.39	2.01	--
APA-6F-BAPB-6F-APA (H2898-59)	160	235	1000	120	1.39	2.93	--
APA-BFDA-BAPB-BFDA-APA Thermid 600 (H2898-53)	140	250	1000	120	1.37	2.70	Advanced resin 45 minutes at 177°C
APA-BFDA-APA Thermid 600 (H2898-55)	25	250	1000	120	1.37	2.83	Advanced resin 45 minutes at 177°C
APA-6F-APA Thermid 600 (H2898-57)	120	240	1000	120	1.38	2.23	Advanced resin 15 minutes at 177°C
APA-6F-BAPB-6F-APA Thermid 600 (H2898-59)	95	250	1000	120	1.38	2.97	Advanced resin 60 minutes at 177°C

* Blending of 1 part of reactive diluent and 2 parts of Thermid 600 was achieved by ball milling using acetone as suspension medium, dried 4 hours at 160°F in air circulating oven.

** Post cure cycle: From room temperature to 450°F within 30 minutes; hold 2 hours at 450°F; increase temperature to 600°F in 2 hours; hold for 4 hours, increase to 700°F in 2 hours; hold for 8 hours at 700°F. Cool slowly. Entire cycle in air atmosphere.

TABLE III. DSC AND TMA DATA FOR NEAT REACTIVE DILUENTS

Resin Description and Ledger I.D. #	M.P. °C	DSC Data		TMA Data		
		EXO Begins °C	EXO Max °C	Cure Conditions °C	Exp. Coef x10 ⁶	Tg °C After Postcure
APA-6F-APA H2898-76, 57, 46	184-186	165	190	250/2 hrs	27	408
APA-6F-BAPB-6F-APA H2898-79, 63, 59, 45, 25	168-178	190	245	250/2 hrs	30	294
APA-BFDA-APA H2898-55	120-122	180	230	372/8 hrs 372/24 hrs	-	312
APA-BFDA-BAPB- BFDA-APA H2898-53	182-185	200	245	250/2 hrs	44	372 225
APA-6F-APA (H2898-57) plus APA-6F-BAPB-6F-APA (H2898-63) 1:1 Mixture	120-130	-	-	250/2 hrs	31	352
6F = 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride BFDA = 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane dianhydride APA = 3-aminophenylacetylene BAPB = 1,3-(3-aminophenoxy)benzene Up to 600°F in 24 hrs. Then up to 700°F. Hold for 8 hours.						

TABLE IV. THERMAL STABILITY OF CURED REACTIVE DILUENTS AND MIXTURES WITH THERMID 600. THERMO GRAVIMETRIC ANALYSIS -3°C/MINUTE IN NITROGEN*

Resin Designation and Ledger I. D. #	Cure Temperature/2 hrs °C	Weight Loss, Percent, When Sample Reached			
		250 °C	400 °C	450 °C	475 °C
APA-6F-APA (H2898-57)	200	1.3	1.4	2.5	4.4
Thermid 600 and H2898-57 1:1 w/w Mixture 2:1 w/w Mixture	200 235	0.9 0.5	1.0 0.8	2.0 2.0	3.5 3.6
APA-6F-BAPB-6F-APA (H2898-59)	255	0.6	0.9	2.5	5.0
Thermid 600 and H2898-59 2:1 w/w Mixture	255	1.1	1.4	2.4	4.0
APA-BFDA-BAPB-BFDA-APA (H2898-53)	250	0.2	0.7	2.8	5.3
Thermid 600 and H2898-53 1:1 w/w Mixture	250	0.75	1.1	2.1	3.8
DSC run on these samples showed no transitions. * Postcured to 316°C (600 °F)					

TABLE V. LONG TERM OXIDATIVE STABILITY OF LAMINATES MADE FROM
REACTIVE DILUENTS AND 1:2 MIXTURES WITH THERMID 600 ***

Resin Description and Ledger I. D. #	Molding Temperature (2 Hours) °C (°F)	Resin Content Wt %	Weight Loss % During Long Term Exposure to 316°C (600 °F) In Air		
			500 Hrs	750 Hrs	1000 Hrs
APA-6F-APA (H2898-57)	200 (392)	25.37	4.41	6.27	17.52
APA-6F-BAPB-6F-APA (H2898-59)	230 (446)	33.73	5.12	8.65	12.68
(H2898-63)*	250 (482)	28.50	1.46	2.40	5.20
APA-BFDA-BAPB-BFDA-APA (H2898-53)	210 (410)	23.01	5.03	9.73	18.21
1:1 MIXTURE OF APA-6F-APA APA-6F-BAPB-6F-APA H2898-57 and 63	225 (437)	27.12	3.22	5.62	8.07
2:1 MIXTURE THERMID 600 and APA-6F-BAPB-6F-APA (H2898-63)	235 (455)	26.71	6.60	12.40	18.58
Thermid 600	250 (482)	32	7.20	16.43	27.72

All specimens post-cured to 700 °F and held at 700 °F for 8 hrs. in air with the exception of * which was cured for 24 hours at 700 °F. - 6 Ply laminates

**Prepreg used 7781 cloth with CS290 finish. Acetone was used as a solvent. In the case of the 2:1 mixture with Thermid and H2898-63, a slurry in acetone was used.

TABLE VI. THERMO MECHANICAL PROPERTIES OF REACTIVE DILUENT
APA-6F-BAPB-6F-APA (H2898-63) AS A CONSEQUENCE
OF THERMAL AGING IN AIR AT 600°F (316°C)

Time in Aging At 600°F (316°C) (Hours)	Weight Loss (Percent)	Flexural Strength		Flexural Modulus	
		Room Temperature psi x 10 ⁻³	316°C (600°F) psi x 10 ⁻³	Room Temperature psi x 10 ⁻⁶	316°C (600°F) psi x 10 ⁻⁶
Control	-	81.1	47.4	3.5	2.7
500	1.46	48.9	56.9	3.6	3.3
750	2.40	41.0	40.8	3.2	2.8
1000	5.20	29.4	33.3	2.9	2.9
1450	9.19	24.1	27.1	2.7	2.6
Laminate: Resin content, 28.50 percent; density, 2.03 gms/cc; void content, 0.63 percent, Tg = 320°C (608°F); molding temperature, 250°C (482°F)/2 hours; glass cloth, 7781-CS-290.					
Post Cure Cycle: To 371°C (700°F) and hold 24 hours at 371°C in air atm. This time determined by measuring Tg as a function of time (up to 36 hours) at 371°C on aliquot portions of this laminate.					

The laminates were prepared using vacuum bag techniques for two hours at 200 psi and 250°C in a preheated press. The four panels were then postcured in air to 372°C and held for eight hours at that temperature. The average resin content of the control panels was 38.3 percent and the resin content of the Thermid 600/reactive diluent was 34.6 percent. Weight losses on cure were 2.53 and 1.39 percent, respectively. One laminate of each of the two compositions was cut into test coupons of 1/2 inch x 3 inches for exposure to 95 percent relative humidity at 80°C (176°F).

Humidity exposure tests (80°C (176°F) at 95 percent relative humidity) and thermal aging tests in air at 600°F (316°C) were completed for both Thermid 600 and Thermid 600/reactive diluent for unidirectional composites made with Thornel 300 graphite fibers. The results of the 30-day humidity exposure test are shown in Table VII. Both the Thermid 600 control and the mixture showed similar trends. The room temperature strength and modulus increased; whereas, the 600°F (316°C) strength decreased by about one-third and the modulus remained the same for the mixture and dropped 10 percent for the control. The 1000-hour thermal aging in air at 600°F (316°C) showed large losses for both the Thermid 600 control and the mixture of the diluent and Thermid 600 as shown in Table VIII. It is significant that the final weight loss after 1000 hours for the Thermid 600 and the mixture of diluent and Thermid 600 were 42.5 and 47.8 percent, respectively which is higher than the 38.3 percent resin content of the composites before the start of the aging test. It is also significant that the composites still exhibited respectable properties. Evidently, the graphite fibers are losing weight at 600°F due to either incomplete graphitization, oxidation or both. Some of our Independent Research and Development work with Thermid 600 using AS graphite fibers shows similar weight losses (45-50 percent). Both these fibers have flexural modules of about 30 MPsi. These fibers are not completely graphitized fibers and could be losing mass at the 600°F aging temperatures so that accelerated oxidation of the resin can take place due to the increase in surface area. This is borne out by the fact that the highest modulus fiber examined, Celanese Corp. GY-70, exhibited a weight loss of only 6-7 percent after 1000-hour exposure at 600°F. Some intermediate modulus fibers, such

TABLE VII. THERMAL MECHANICAL PROPERTIES OF 2:1 MIXTURE OF THERMID 600 AND REACTIVE DILUENT APA-6F-BAPB-6F-APA (H2898-80) AS A CONSEQUENCE OF HUMIDITY AGING (95 PERCENT RELATIVE HUMIDITY, 80°C 176°F)

Time in Aging 80°C, 95% RH (Days)	Thermid 600			2:1 Thermid 600/H2898-80		
	Weight Increase (Percent)	Room Temp.	600°F (316°C)	Weight Increase (Percent)	Room Temp.	600°F (316°C)
		Flex. Strength x 10 ⁻³ / Flex. Mod. x 10 ⁻⁶ psi			Flex. Strength x 10 ⁻³ / Flex. Mod. x 10 ⁻⁶ psi	
0	0	181/14.4	155/14.7	0	184/13.6	144/11.9
15	1.21	180/13.1	103/11.5	0.94	190/13.6	99/11.4
30	1.49	197/16.6	109/12.4	1.19	199/17.1	96/12.5
<p>Laminate: Thermid 600, 38.3 percent resin content, Thornel 300 unidirectional fiber, molding temperature, 250°C/2 hours, postcured to 372°C cycle-held at 372°C for 8 hours in air.</p> <p>Thermid 600/APA-6F-BAPB-6F-APA (H2898-80), 34.6 percent resin content, Thornel 300 unidirectional fiber. Molding temperature and post-cure same as above.</p> <p>The flexural strengths and moduli were determined by testing the coupons immediately after removal from the humidity chamber with no soak time.</p>						

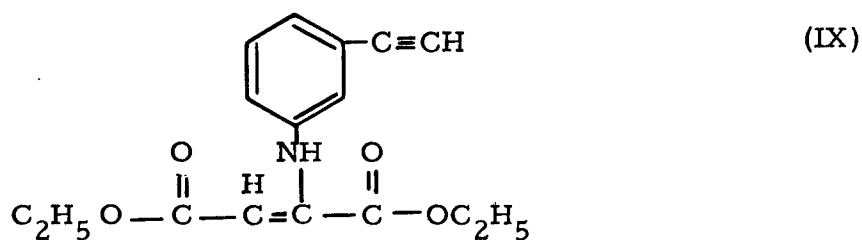
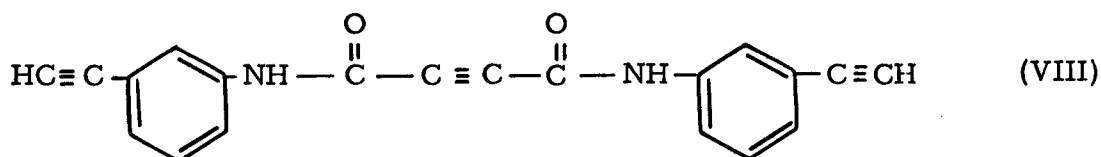
TABLE VIII. THERMAL MECHANICAL PROPERTIES OF 2:1 MIXTURE OF THERMID 600 AND REACTIVE DILUENT APA-6F-BAPB-6F-APA (H2898-80) AS A CONSEQUENCE OF THERMAL AGING IN AIR AT 600°F (316°C)

Hours	Thermid 600			2:1 Thermid 600/H2898-80		
	Weight Loss (Percent)	Room Temp.	600°F (316°C)	Weight Loss (Percent)	Room Temp.	600°F (316°C)
		Flex. Strength x 10 ⁻³ / Flex. Mod. x 10 ⁻⁶ psi			Flex. Strength x 10 ⁻³ / Flex. Mod. x 10 ⁻⁶ psi	
0	0	181/14.4	155/14.7	0	184/13.6	144/11.9
125	0.64	157/15.0	165/15.0	0.62	159/15.4	150/14.6
250	1.38	166/13.7	165/14.1	1.92	131/13.4	100/12.1
500	8.8	124/12.9	115/11.3	11.01	88/9.6	102/10.9
750	16.9	89/9.1	103/9.2	22.47	58/6.0	63/6.1
1000	42.5	60/5.9	77/8.4	47.77	34/3.6	45/4.4
Laminate: Thermid 600, 38.3 percent resin content, Thornel 300 unidirectional fiber. Molding temperature, 250°C/2 hours, post-cured to 372°C cycle-held at 372°C for 8 hours in air.						
Thermid 600/APA-6F-BAPB-6F-APA (H2898-80), 34.6 percent resin content. Thornel 300 unidirectional fiber. Molding temperature and post-cure same as above.						

as the HTS and HMS, 40 and 50 MPa modulus fibers, respectively, made by Hercules, exhibited weight losses of 10-15 percent.

Thermal mechanical properties were collected on a unidirectional panel made from a 2:1 w/w mixture of Thermid 600 and APA-BFDA-APA (Lot H2898-91) using HTS fiber since we have found this fiber to be superior to Thornel 300 in thermal aging of 600°F. The panel was aged in air at 600°F (316°C) for 1000 hours. The thermal mechanical properties are shown in Table IX. The thermal aging tests show that the degradation starts to accelerate somewhere between 250-500 hours. Further postcure studies are required to optimize the thermal stability of the Thermid 600/Reactive Diluent mixture.

Early in the program we attempted to prepare a diluent by the reaction of 2 moles of 3-aminophenylacetylene with 1 mole of diethylacetylenedicarboxylate to yield N, N'-(bis-3-ethynylphenyl)acetylenedicarboxamide (VIII.). However, a crystalline compound was isolated whose molecular weight and elemental analysis were consistent with the formula depicted by IX.



The DSC of IX is shown in Figure 5, which shows that it has a maximum exotherm at 217°C. Although this is a low melting diluent, the presence of ethoxy groups could lead to the evolution of ethanol during cure. Continuation of studies on this diluent were discontinued.

Another approach which was investigated involved the use of a reactive diluent which was less reactive than the HR600, but which, nevertheless, can

TABLE IX. THERMAL MECHANICAL PROPERTIES OF 2:1 MIXTURE OF THERMID 600 AND REACTIVE DILUENT APA-BFDA-APA (H2898-91) AS A CONSEQUENCE OF THERMAL AGING IN AIR AT 600°F (316°C)

Hours	Weight Loss (Percent)	2:1 Thermid 600/H2898-80	
		Room Temp.	600°F (316°C)
		Flex. Strength x 10 ⁻³ /Flex. Modulus x 10 ⁻⁶ psi	
0	0	200/14.6	135/15.5
250	1.83	187/14.3	153/14.8
500	10.34	113/10.8	97/8.7
750	17.20	a	a
1000	17.30	a	a
Laminate: Thermid 600 (Lot 7D106)/APA-BFDA-APA (H2898-91), 34.5 percent resin content, HTS unidirectional fiber (56-4). Molding temperature, 250°C/2 hours, post-cured to 372°C cycle-held at 372°C for 8 hours in air. a: Not tested due to excessive surface degradation of laminate.			

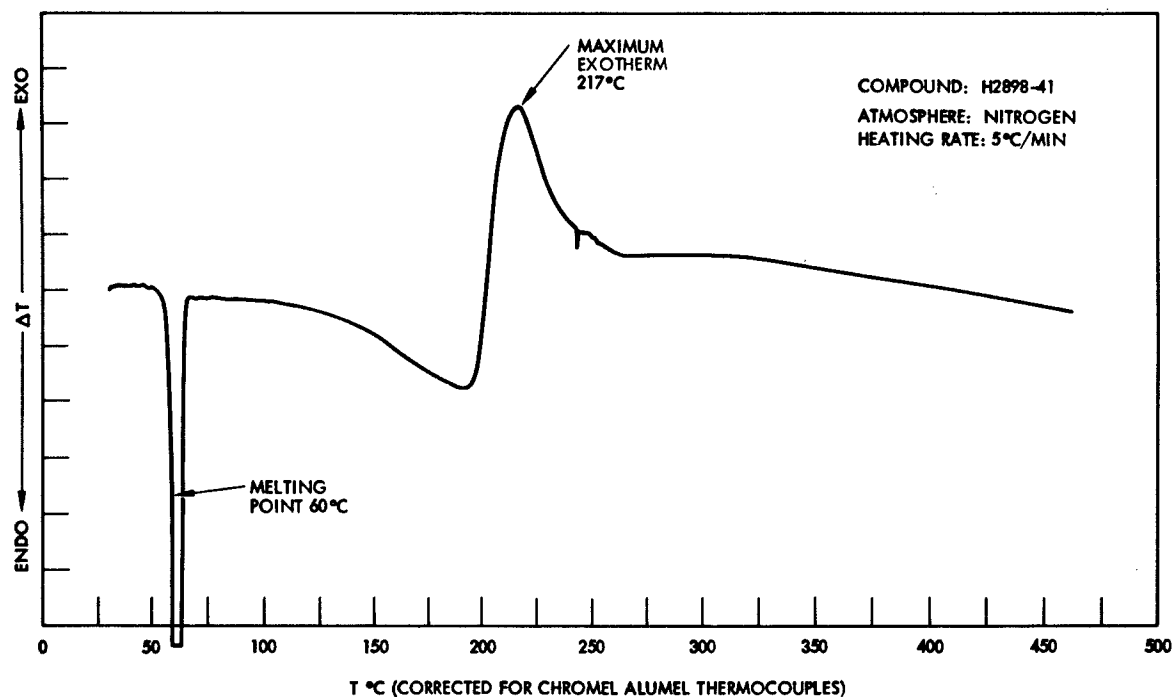
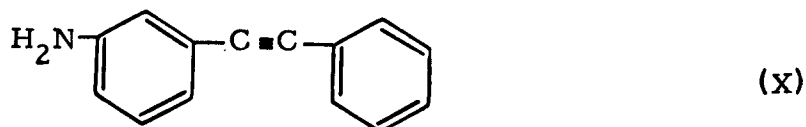


Figure 5. DSC of reaction product between 3-aminophenylacetylene and diethyl acetylenedicarboxylate.

homopolymerize. The intermediate, 3-aminodiphenylacetylene (X) was prepared. Although NMR data were consistent with structure X, elemental



analysis shows it to contain about 15 percent 3-iodoaniline. This batch, which was 85 percent pure, was used for the preparation of a small amount of HR600 type oligomer substituting this intermediate (X) for the 3-aminophenylacetylene. The oligomer, which melted at $145^\circ - 155^\circ\text{C}$, did not cure. However, this may possibly be attributed to the fact that non-reactive terminal groups were present. The study was postponed at this time until the perfluoroisopropylidene substituted diluents are more thoroughly explored.

Since liquid ranges for the resin/diluent mixtures can be formulated to yield melting ranges considerably below 200°C , the melting range for the pure HR600 oligomer and the temperature above which homopolymerization

proceeds at a reasonable rate as shown by differential thermal analysis (DTA), we are ready to look at catalysts as a means of accelerating the cure rate at temperatures below 200°C. The most promising catalyst is bis(benzonitrile) palladium dichloride. This catalyst has been found to accelerate the homopolymerization of the HR600 and HR602 oligomers, as evidenced by a drop in gel time at 224°C for both oligomers after treating the resins at 60°C with 0.2 weight percent of catalyst. In one case where HR600 was treated with 3 weight percent of the catalyst, the resin did not melt while heated to above its normal melting point, indicating that homopolymerization had taken place at an enhanced rate below the normal melting range (190 - 200°C) of the oligomer. Thus, with a lower melting oligomer, the desired low temperature cures may be possible.

2. Titanium Adhesive Studies

Our previous studies have shown that the HR602 type oligomer is most suitable as a one-component adhesive for 6Al 4V titanium rather than HR-600 or HR-603. Our earlier work showed that, in order to achieve the best overall strength, it was necessary to use mixtures of meta-cresol/benzene and acetic anhydride imidized oligomers. Otherwise poor adhesion at elevated temperatures resulted. Our work with these resins showed also that it is extremely difficult to remove the last traces of meta-cresol from the meta-cresol/benzene imidization product as well as the dimethylformamide (DMF) used as a solvent to prepare the polyamic acid precursor. Temperatures up to 600°F (316°C), well above the cure temperature, are required for removal of the last traces of these solvents. Solvent is thus entrapped in the resin matrix and causes a blistering during elevated temperature exposure. The entrapped DMF and meta-cresol could cause premature failure of the adhesive bond, particularly at the higher temperatures. It was found that much lower solvent entrapment results by using NMP along with benzene as an imidizing solvent pair. Thus, this present study uses oligomers prepared in a manner which excludes DMF and meta-cresol. NMP is more easily removed from the prepolymer.

Thus, the synthesis of these polyimides entails the following:

1. The preparation of polyamic acid
2. Imidization of the polyamic acid by a number of routes, namely
 - a. Use of meta-cresol/benzene
 - b. NMP/benzene
 - c. Acetic anhydride
 - d. Trifluoroacetic anhydride

Our earlier study with acetic anhydride imidized HR-602 showed that some of the acetic anhydride probably reacted with the amic acid during the course of imidization to give a mixed acid anhydride. Depending upon the concentration, the presence of large amounts of mixed acid anhydrides lowered high temperature lap shear strengths of titanium bonded specimens. Substitution of trifluoroacetic anhydride for acetic anhydride gave more consistent results.

In order to learn the effects of different techniques of imidization, titanium lap shear studies were carried out on three batches of oligomer, with different imidization conditions for each. The first was imidized in NMP-benzene (No. H2350-88A), the second in trifluoroacetic anhydride (No. H2350-88B), and the third in acetic anhydride (No. H2350-95).

The mixtures used were the following:

1. 50:50 mixture of NMP/Benzene and Trifluoroacetic Anhydride
2. 50:50 mixture of NMP/Benzene and Acetic Anhydride
3. NMP/Benzene

In the past we found that residual solvent entrapped in the prepreg influences bond strength. Most of the solvent can be removed using a preliminary drying cycle employing heat. Since heat also advances the prepreg, which affects strength, a tradeoff must be made for the degree of advancement and degree of dryness. The effect of additional drying on a 50:50 mixture of HR602 imidized in NMP-benzene and in trifluoroacetic anhydride is shown in Table X. Prepreg A appears somewhat overadvanced in the initial drying, as indicated by the observed maximum strength with no additional drying at 325°F (163°C). Prepreg B, which received less severe preliminary drying, shows better strengths after 30 and 45 minutes additional drying at 325°F.

**TABLE X. ROOM TEMPERATURE LAP SHEAR STRENGTHS,
50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE
AND IN TRIFLUOROACETIC ANHYDRIDE**

Additional Drying Time, Minutes at 325°F (163°C)	Cure 600°F (316°C) for 4 Hours		Cure 550°F (288°C) for 2 Hours, 600°F (316°C) for 2 Hours	
	Lap Shear Strength, psi x 10 ⁻³	Failure Mode	Lap Shear Strength, psi x 10 ⁻³	Failure Mode
Prepreg A				
0	3.38±0.07	CO	2.14±0.21	AD
15	2.88±0.21	CO	1.32±0.14	AD
30	2.18±0.30	CO/AD	1.24±0.21	AD
45	1.92±0.28	CO/AD	1.28±0.30	AD
Prepreg B				
0	2.70±0.04	CO	-	-
15	2.80±0.15	CO	2.78±0.14	CO
30	3.48±0.08	CO	2.92±0.22	CO/AD
45	3.43±0.23	CO/AD	2.64±0.17	CO/AD
60	3.06±0.19	CO	-	-
<p>Prepreg A 112E glass cloth, heat cleaned, resin content 70 wt % dried at 350°F (177°C) for 30 minutes</p> <p>Prepreg B 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 300°F (149°C) for 40 minutes</p> <p>HR602 NMP-Benzene Imidized - Resin No. H2350-88A</p> <p>HR602 Trifluoroacetic Anhydride Imidized-Resin H2350-88B</p> <p>Titanium cleaned with TURCO alkaline cleaner 5578</p> <p>CO = cohesive AD = adhesive</p> <p>Results are averages for five specimens with average deviation shown.</p>				

The next variable studied was cure cycle. Using the best overall additional drying cycle on prepreg B, two cure programs were used. The first was a 4 hour cure at 600°F (316°C) and the second was a step cure using 2 hours at 550°F (288°C) and 2 hours at 600°F (316°C). The second cure gave lower strengths in general. The best average result was 3,500 psi lap shear strength. Undoubtedly higher values could be realized with an optimized cure. Table XI compares the results obtained for this mixture, again using prepreg B, at ambient temperature, 500°F (260°C), 550°F (288°C), and 600°F (316°C), again using the two cure programs just described. The 600°F cure for 4 hours gave better 500°F (260°C) strengths, but similar strengths at 550°F (288°C), and 600°F (316°C) to the two step cure. The failure mode at the elevated temperatures was adhesive.

The second group of lap shear strength experiments was carried out on a 50:50 mixture of polyamic acid imidized in NMP-benzene (No. H2350-88A) and in acetic anhydride (No. H2350-95). The prepreps were made in a similar manner as in the first series. The results were very similar for the room temperature strengths; however, the high temperature strengths were somewhat better than those of the first group, particularly at 550°F (288°C) and 600°F (316°C). The results are shown in Tables XII and XIII.

The third series of lap shear strengths was obtained on adhesive using only NMP-benzene imidized HR602 (No. H2350-88A). Although the best room temperature results were similar to the results of the other two series, the elevated temperature results were poorer. The results are shown in Tables XIV and XV. In the past, the use of DMF-m-cresol/benzene imidized prepolymer gave poor adhesion at higher temperatures. It was necessary to incorporate acetic anhydride imidized resin to improve adhesion at elevated temperatures. The exact role of the acetic anhydride was not clearly understood, but it did promote improved wetting of the titanium.

Because, in the past, acetic anhydride imidized oligomer tended to be variable in composition due to the formation of mixed anhydride, we decided to restrict ourselves to the use of the trifluoroacetic anhydride imidized oligomer for adhesion improvement.

The adhesive failure mode at elevated temperatures of titanium specimens bonded with HR602 type resins suggests that oxidation may be taking

TABLE XI. LAP SHEAR STRENGTHS AT VARIOUS TEMPERATURES,
50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE
AND IN TRIFLUOROACETIC ANHYDRIDE

Additional Drying Time at 300°F (149°C) minutes	Cure 4 Hrs. at 600°F (316°C)				Cure 2 Hrs. at 550°F (288°C) and Then 2 Hrs. at 600°F (316°C)			
	Lap Shear Strengths, psi x 10 ⁻³				Lap Shear Strengths, psi x 10 ⁻³			
	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)
0	2.7 ± 0.1	-	-	-	-	-	-	-
15	2.8 ± 0.2	-	-	-	2.8 ± 0.2	-	-	-
30	3.5 ± 0.1	-	-	-	2.8 ± 0.2	1.0 ± 0.3	1.2 ± 0.2	0.57 ± 0.08
45	3.4 ± 0.2	1.8 ± 0.2	1.1 ± 0.1	0.6 ± 0.6	2.6 ± 0.2	-	-	-
60	3.1 ± 0.2	-	-	-	-	-	-	-

Prepreg prepared from 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 300°F (149°C) for 40 minutes.

HR602 NMP-Benzene Imidized - Resin No. H2350-88A

HR602 Trifluoroacetic Anhydride Imidized - Resin No. H2350-88B

Titanium cleaned with TURCO alkaline cleaner 5578.

Results are averages for five specimens with average deviation shown.

All specimens soaked at temperature 30 minutes prior to test.

TABLE XII. ROOM TEMPERATURE LAP SHEAR STRENGTHS,
50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE
AND IN ACETIC ANHYDRIDE

Additional Drying Time, Minutes at 325°F (163°C)	Cure 600°F (316°C) for 4 Hours		Cure 550°F (288°C) for 2 Hours, 600°F (316°C) for 2 Hours	
	Lap Shear Strength, psi x 10 ⁻³	Failure Mode	Lap Shear Strength, psi x 10 ⁻³	Failure Mode
Prepreg A				
0	2.26±0.81	AD	2.70±0.24	CO/AD
15	2.15±0.40	AD	1.92±0.28	AD
30	1.60±0.24	AD	1.88±0.07	AD
45	1.82±0.14	AD	1.86±0.15	AD
Prepreg B				
15	3.14±0.11	CO	2.94±0.16	CO
30	3.14±0.11	CO	2.70±0.08	CO
45	3.20±0.20	CO	2.76±0.17	CO/AD
<p>Prepreg A 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 350°F (177°C) for 30 minutes</p> <p>Prepreg B 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 300°F (149°C) for 25 minutes</p> <p>HR602 NMP-Benzene Imidized - Resin No. H2350-88A</p> <p>HR602 Acetic Anhydride Imidized - Resin No. H2350-95</p> <p>Titanium cleaned with TURCO alkaline cleaner 5578</p> <p>CO = cohesive; AD = adhesive</p> <p>Results are averages for five specimens with average deviation shown.</p>				

TABLE XIII. LAP SHEAR STRENGTHS AT VARIOUS TEMPERATURES,
50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE
AND IN ACETIC ANHYDRIDE

Additional Drying Time at 325°F (163°C) minutes	Cure 4 Hrs. at 600°F (316°C)				Cure 2 Hrs. at 550°F (288°C) and Then 2 Hrs. at 600°F (316°C)			
	Lap Shear Strengths, psi x 10 ⁻³				Lap Shear Strengths, psi x 10 ⁻³			
	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)
15	3.1 ± 0.2	-	-	-	2.9 ± 0.1	2.0 ± 0.1	1.3 ± 0.3	0.95 ± 0.05
30	3.1 ± 0.1	-	-	-	2.7 ± 0.1	-	-	-
45	2.6 ± 0.2	1.9 ± 0.2	1.3 ± 0.2	1.0 ± 0.1	2.8 ± 0.2	-	-	-
Prepreg prepared from 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 300°F (149°C) for 25 minutes								
HR602 NMP-Benzene Imidized - Resin No. H2350-88A								
HR602 Acetic Anhydride Imidized - Resin No. H2350-95								
Titanium cleaned with TURCO alkaline cleaner 5578.								
Results are averages for five specimens with average deviation shown.								
All specimens soaked at temperature for one-half hour prior to test.								

TABLE XIV. ROOM TEMPERATURE LAP SHEAR STRENGTHS
OF HR602 IMIDIZED IN NMP-BENZENE

Additional Drying Time, Minutes at 325°F (163°C)	Cure 600°F (316°C) for 4 Hours		Cure 550°F (288°C) for 2 Hours, 600°F (316°C) for 2 Hours	
	Lap Shear Strength, psi x 10 ⁻³	Failure Mode	Lap Shear Strength, psi x 10 ⁻³	Failure Mode
Prepreg A				
0	2.84 ± 0.25	CO/AD	1.54 ± 0.09	AD
15	1.70 ± 0.24	CO/AD	1.12 ± 0.10	AD
30	1.40 ± 0.16	CO/AD	1.44 ± 0.14	AD
45	1.48 ± 0.10	AD	1.18 ± 0.34	AD
Prepreg B				
15	3.10 ± 0.20	CO	2.52 ± 0.26	CO/AD
30	3.08 ± 0.08	CO	2.38 ± 0.26	CO/AD
45	2.56 ± 0.21	CO/AD	1.90 ± 0.32	AD
<p>Prepreg A 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 350°F (177°C) for 30 minutes</p> <p>Prepreg B 112E glass cloth, heat cleaned, resin content 70 wt %, dried at 300°F (149°C) for 30 minutes</p> <p>HR602 NMP-Benzene Imidized - Resin No. H2350-88A</p> <p>Titanium cleaned with TURCO alkaline cleaner 5578</p> <p>CO = cohesive; AD = adhesive</p> <p>Results are averages for five specimens with average deviation shown.</p>				

TABLE XV. LAP SHEAR STRENGTHS AT VARIOUS TEMPERATURES
OF HR602 IMIDIZED IN NMP-BENZENE

Additional Drying Time at 325°F (163°C) Minutes	Cure 4 Hrs. at 600°F (316°C)				Cure 2 Hrs. at 550°F (288°C) and Then 2 Hrs. at 600°F (316°C)			
	Lap Shear Strengths, psi x 10 ⁻³				Lap Shear Strengths, psi x 10 ⁻³			
	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)	R. T.	500°F (260°C)	550°F (288°C)	600°F (316°C)
15	3.1 ± 0.2	-	-	-	2.5 ± 0.3	1.1 ± 0.1	0.93 ± 0.30	0.49 ± 0.11
30	3.1 ± 0.1	1.0 ± 0.1	0.62 ± 0.19	0.46 ± 0.13	2.4 ± 0.3	-	-	-
45	2.6 ± 0.2	-	-	-	1.9 ± 0.3	-	-	-

Prepreg prepared from 112E glass cloth, resin content 70 wt %, dried at 300°F (149°C) for 30 minutes.

HR602 NMP-Benzene Imidized - Resin No. H2350-88A

Titanium cleaned with TURCO alkaline cleaner 5578.

Results are averages for five specimens with average deviation shown.

All specimens soaked for one-half hour at temperature prior to test.

place at the resin-titanium interface and that an antioxidant may improve bonding. To test out this hypothesis, we prepared three prepregs using a 50:50 mixture of HR602 NMP-benzene imidized resin (H2898-21) and HR602 trifluoroacetic anhydride imidized resin (H2898-22B), adding 10, 25 and 50 weight percent aluminum based on resin weight. The results are shown in Tables XVI, XVII and XVIII. A shorter cure was used (600°F for 2 hours) than the 4 hour cure at 600°F for the earlier series. There was a slight dropoff in room temperature strength (2900 psi versus 3500 psi) as a result of incorporating aluminum.

In order to determine the optimum cure, a detailed study was completed on the effect of cure parameters on lap shear strength of titanium specimens bonded with a prepreg consisting of HR602 on a 112E heat cleaned glass cloth. The results for both filled and unfilled prepregs are shown in Tables XIX and XX. The series using cures at 700°F for 2 hours and at 600°F for 16 hours was completed during this period while the other data were taken from previous work on this program. Very high temperature cures, such as the 700°F (371°C) 2 hour cure, were found to lower the ambient temperature strengths as compared to 600°F (316°C) cure at comparable cure time. There does not appear to be too much difference between 25 and 50 weight percent aluminum powder as a filler. Comparison of the results of the filled and unfilled prepreg does not support the use of aluminum as a filler for improved high temperature lap shear strengths. It can be seen that the lap shear strengths at 550°F for both the filled and unfilled prepregs are comparable. There is insufficient data at 600°F to evaluate the effectiveness of aluminum as a filler at this time. The most important consideration is the cure cycle. To realize the best high temperature values, sufficient time at 600°F is required. Both the filled (prepregs A and B) and unfilled (prepregs C and D) samples clearly show this trend at 500°F lap shear strengths. About 8 hours at 600°F appears to be an optimum cure for 550°F degree exposure temperature. However, for exposure temperatures up to 500°F , 4 hours at 600°F appears to be adequate. For 450°F temperature exposure, 2 hour cure at 600°F seems to be adequate.

TABLE XVI. ROOM TEMPERATURE LAP SHEAR STRENGTHS,
50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE AND
IN TRIFLUOROACETIC ANHYDRIDE AND CONTAINING
10 wt % ALUMINUM

Additional Drying Time, Minutes at 325°F (163°C)	Cure 600°F (316°C) for 2 Hours	
	Lap Shear Strength, psi x 10 ⁻³	Failure Mode
0	2.84 ± 0.05	CO/AD
15	2.76 ± 0.13	CO/AD
30	2.84 ± 0.05	CO/AD
45	2.92 ± 0.09	CO/AD
<p>112E glass cloth, heat cleaned, resin content 60 wt %, 10 wt % of aluminum (325 mesh) based on resin, dried at 300°F for 25 minutes</p> <p>HR602 NMP-Benzene Imidized - Resin No. H2898-21</p> <p>HR602 Trifluoroacetic Anhydride Imidized - Resin No. H2898-22B</p> <p>Titanium cleaned with TURCO alkaline cleaner 5578</p> <p>CO = cohesive; AD = adhesive</p> <p>Results are averages for five specimens with average deviation shown.</p>		

TABLE XVII. LAP SHEAR STRENGTHS AT ROOM TEMPERATURE AND 500°F (260°C), 50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE AND IN TRIFLUOROACETIC ANHYDRIDE AND CONTAINING 25 wt % ALUMINUM

Additional Drying Time, Minutes at 325°F (163°C)	Cure at 600°F (316°C) 2 Hours			
	Room Temperature Lap Shear Strength, psi x 10 ⁻³	Failure Mode	500°F (260°C) Lap Shear Strength, psi x 10 ⁻³	Failure Mode
0	2.75 ± 0.05	CO/AD	-	-
15	2.79 ± 0.06	CO/AD	-	-
30	2.87 ± 0.04	CO/AD	1.64 ± 0.18	CO/AD
45	2.88 ± 0.07	CO/AD	-	-

112E glass cloth, heat cleaned, resin content 70 wt %, 25 wt % of aluminum (325 mesh) based on resin, dried at 300°F for 25 minutes

HR602 NMP-Benzene Imidized - Resin No. H2898-21

HR602 Trifluoroacetic Anhydride Imidized - Resin No. H2898-22B

Titanium cleaned with TURCO alkaline cleaner 5578

CO = cohesive; AD = adhesive

Results are averages for five specimens with average deviation shown.

All specimens soaked for one-half hour at temperature prior to test.

TABLE XVIII. LAP SHEAR STRENGTHS AT ROOM TEMPERATURE AND 500°F (260°C), 50:50 MIXTURE OF HR602 IMIDIZED IN NMP-BENZENE AND IN TRIFLUOROACETIC ANHYDRIDE AND CONTAINING 50 wt % ALUMINUM

Additional Drying Time, Minutes at 325°F (163°C)	Cure at 600°F (316°C) 2 Hours			
	Room Temperature Lap Shear Strength, psi x 10 ⁻³	Failure Mode	500°F (260°C) Lap Shear Strength, psi x 10 ⁻³	Failure Mode
0	2.65 ± 0.07	CO/AD	-	-
15	2.90 ± 0.06	CO/AD	1.56 ± 0.06	CO/AD
30	2.86 ± 0.07	CO/AD	-	-
45	2.83 ± 0.17	CO/AD	-	-

112E glass cloth, heat cleaned, resin content 67.4 percent, 50 wt % of aluminum (325 mesh) based on resin, dried at 300°F for 25 minutes

HR602 NMP-Benzene Imidized - Resin No. H2898-21

HR602 Trifluoroacetic Anhydride Imidized - Resin No. H2898-22B

Titanium cleaned with TURCO alkaline cleaner 5578

CO = cohesive; AD = adhesive

Results are averages for five specimens with average deviation shown.

All specimens soaked at temperature for one-half hour prior to test.

TABLE XIX. LAP SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH ALUMINUM FILLED HR-602 PREPREG

	Cure		Lap Shear Strengths (Results are averages for five specimens)					
			R. T.		500°F		550°F	
	Time Hours	Temp °F	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode
Prepreg A 25 wt percent Al Filled	2	700	1.98	CO/AD	1.80	CO/AD	1.42	CO/AD
	1	600	-	-	1.00	CO/AD	-	-
	2	600	2.87	CO/AD	1.64	CO/AD	-	-
	3	600	-	-	1.23	CO/AD	-	-
	4	600	-	-	1.44	CO/AD	-	-
	6	600	-	-	1.74	CO/AD	-	-
	8	600	-	-	1.79	CO/AD	-	-
	10	600	-	-	1.84	CO/AD	-	-
	16	600	2.70	CO/AD	2.03	CO/AD	1.45	CO/AD
	16	600	-	-	1.77	CO/AD	-	-
Prepreg B 50 wt percent Al Filled	2	700	2.00	CO/AD	1.66	CO/AD	1.34	CO/AD
	1	600	-	-	0.90	CO/AD	-	-
	2	600	2.90	CO/AD	1.56	CO/AD	-	-
	3	600	-	-	1.31	CO/AD	-	-
	4	600	-	-	1.48	CO/AD	-	-
	6	600	-	-	1.49	CO/AD	-	-
	8	600	-	-	1.62	CO/AD	-	-
	10	600	-	-	1.66	CO/AD	-	-
	16	600	-	-	1.98	CO/AD	1.39	CO/AD
<p>Prepreg A: 112E Glass Cloth, heat cleaned, resin content 70 wt. percent; 25 wt. percent of aluminum (325 mesh) based on resin, dried at 300°F for 25 minutes - Resins 50:50 mixture of HR-602 NMP/BZ Lot H2898-21 and HR-602 Trifluoroacetic Anhydride Imidized. Lot H2898-22B-Additional Drying Time 30 minutes at 325°F.</p> <p>Prepreg B: 112E Glass Cloth, heat cleaned, resin content 67.4 wt. percent, 50 wt. percent of aluminum (325 mesh) based on resin dried at 300°F for 25 minutes - Resins 50:50 mixture of HR-602 NMP/BZ Lot H2898-21 and HR-602 Trifluoroacetic Anhydride Imidized. Lot H2898-22B-Additional Drying Time 15 minutes at 325°F.</p> <p>CO = Cohesive; AD = Adhesive; Titanium cleaned with TURCO Alkaline Cleaner 5578</p> <p>Specimens soaked for one-half hour at temperature prior to test.</p>								

TABLE XX. LAP SHEAR STRENGTH OF TITANIUM SPECIMENS BONDED
WITH HR-602 PREPREG

	Prepreg Additional Drying at 350°F (177°C)	Cure		R. T.		450°F		500°F		550°F		600°F	
		Time Hours	Temp °F	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode	psi x 10 ⁻³	Failure Mode
Prepreg C	0	4	600	3.40	CO	-	-	1.80	CO/AD	1.10	CO/AD	0.60	AD
Prepreg D	0	2	600	2.76	CO	2.24	CO/AD	-	-	-	-	-	-
	10	2	600	3.43	CO	2.20	CO/AD	-	-	-	-	-	-
	20	2	600	3.30	CO	2.20	CO/AD	-	-	-	-	-	-
	0	4	600	3.02	CO	2.36	CO/AD	1.79	CO/AD	1.15	CO/AD	-	-
	10	4	600	2.82	CO	2.51	CO/AD	-	-	-	-	-	-
	20	4	600	2.79	CO	2.48	CO/AD	-	-	-	-	-	-
Prepreg E	0	8	600	3.10	CO	2.39	CO/AD	2.05	CO/AD	1.70	CO/AD	-	-
	0	16	600	2.76	CO	2.51	CO/AD	2.15	CO/AD	1.63	CO/AD	-	-
<p>Prepreg C: 112E Glass Cloth, heat cleaned, resin content 70 wt. percent, no filler - Resin 50:50 mixture of HR602 NMP/EZ Lot H2898-21 and HR602 Trifluoroacetic Anhydride Imidized Lot H2898-22B. Dried at 300°F for 40 minutes.</p> <p>Prepreg D: 112E Glass Cloth, heat cleaned, resin content 68 wt. percent, no filler - Resin 50:50 mixture of HR602 NMP/EZ Lot H2898-68A and HR602 Trifluoroacetic Anhydride Imidized Lot H2898-68B. Dried at 300°F for 30 minutes.</p> <p>CO = Cohesive AD = Adhesive Titanium cleaned with TURCO alkaline cleaner 5578 Results are averages for five specimens. Specimens soaked for one-half hour at temperature prior to test.</p>													

The drop-off in properties at elevated temperatures appears to be due to the increase in adhesive failure mode. Evidently further work is required to obtain a more optimum surface for retention of adhesive strength. Also, small traces of volatiles given off during the curing cycle as a consequence of solvent inclusion could prevent the achievement of a void-free interface. The use of hot melt prepregs may be required to minimize this problem.

3. Titanium Honeycomb Structures

Titanium honeycomb specimens were prepared, using 3/4-inch titanium honeycomb between 50 mil 6 Al 4V titanium sheets. The honeycomb had 1/4-inch cells of 4 to 4.5 mil foil and holes perforated between each cell to allow for escape of gases. The titanium was etched with the TURCO alkaline bath before assembly. Results of the Pi-Tension Honeycomb tests are shown in Table XXI.

TABLE XXI. PI-TENSION TENSILE STRENGTHS OF
TITANIUM HONEYCOMB SPECIMENS

Honeycomb Specimen	Ambient Temperature Tensile Strength psi	Remarks
-1	143	Filleting
-2	110	Filleting
-3	143	Filleting
<p>NOTES: (1) Honeycomb specimens were prepared and tested in accordance with General Dynamics Corp. Specification FMS-1013.</p> <p>(2) Heat-cleaned glass cloth 112E was employed as a reinforcement using a 50:50 resin mixture of HR 602 NMP/BZ lot H2898-68A and HR602 Trifluoroacetic Anhydride Imidized H2898-68B. Dried at 300°F for 30 minutes.</p> <p>(3) Prepared using 15 psi pressure on titanium faces in a 600°F press for 8 hours.</p>		

4. Weldbonding

Weldbond schedules have been established for spotwelding of titanium specimens and both spotwelded and weldbonded specimens have been prepared. All spotwelded lap shear specimens had a 1-inch overlap. The weldbond titanium specimens were cleaned with TURCO 5578 alkaline cleaner. The weldbond specimens used a hot melt mixture. Weld schedules were established on three phase Sciaky Spot Welders with solid state controllers, and both spotwelded and weldbonded specimens were prepared for S/N tests. The weld nugget was centrally located on the overlap and was approximately 1/4-inch diameter. This weld gave about 3000 psi for the lap shear strength. The adhesive mixtures which were employed as a hot melt mixture had the following composition by weight:

Mixture A

APA-BFDA-APA (Lot J1580-14A)	1 part
Aluminum powder 325 mesh	1 part

Mixture B

APA-BFDA-APA (Lot J1580-14A)	1 part
Thermid 600 (Lot 6F402)	1 part
Aluminum powder 325 mesh	2 parts

In order to make these mixtures electrically conductive, the titanium coupons containing the adhesive mixture were clamped with vise grip type pliers and placed on an aluminum top hot plate at about 200°C; when the adhesive was molten, the coupons spotwelded. Using these two formulations, good spotwelds were obtained. The specimens were then cured for 8 hours at 600°F (316°C) in air.

5. S/N Tests

S/N (fatigue) tests were run to evaluate the fatigue life of spotweld bonded titanium specimens, using aluminum filled Thermid 600/APA-BFDA-APA diluent mixture in one case and aluminum filled ABA-BFDA-APA in the other case. These tests were run on 1.0-inch overlap, 0.050-inch thick titanium specimens, 1.0-inch wide. Comparisons were made between adhesive bonded, spot welded, and weldbonded specimens. The bonded

samples were cured in air at 600°F (316°C) for 8 hours. The spot welded specimens were given the same treatment to assure uniformity. The S/N tests on the spotwelded, weldbonded and adhesive bonded specimens are shown in Tables XXII, XXIII, XXIV, XXV and XXVI, and on Figures 7, 8, and 9. The observed failure modes are shown in Figure 6.

One of the most important principles established with these compositions is that we can effectively weldbond through a hot melt without the use of solvent. The reactive diluent lowers the melting range of the Thermid 600 so that the hot melt technique can be used. The reactive diluent/Thermid 600 weldbonded compositions clearly show increased fatigue resistance by about an order of magnitude at the lower load levels over the spotwelded specimens. The adhesive only bonded compositions show excellent fatigue resistance at the lower load levels. However the strength of the adhesive bond is low since no reinforcement was used. The failure modes were nearly all type II or III, involving either metal fatigue or ejection of the weld nugget. The failure for the unwelded specimens showed that the pressure applied to the titanium coupons during the hot melt application resulted in resin starved joints. A study is needed in varying the aluminum mesh size and loading since this can help control the bond line thickness. Also, further development of the welding cycle is needed for these compositions to obtain more reproducible welds.

TABLE XXII. FATIGUE TEST, WELDED TITANIUM
 $F_{TU} = 3120$ LBS, $R = 0$ NO ADHESIVE

Spec. No. J1580-20A	Load Lbs	N Cycles	Failure Mode	Remarks
2	0-2496 ($0.8 F_{TU}$)	180	IV	
3	0-2496 ($0.8 F_{TU}$)	240	IV	
4	0-2496 ($0.8 F_{TU}$)	210	IV	
5	0-2496 ($0.8 F_{TU}$)	180	IV	
17	0-2496 ($0.8 F_{TU}$)	210	III & IV	
6	0-1872 ($0.6 F_{TU}$)	1,095	IV	
7	0-1872 ($0.6 F_{TU}$)	1,515	IV	
8	0-1872 ($0.6 F_{TU}$)	1,650	IV	
9	0-1872 ($0.6 F_{TU}$)	978	IV	
10	0-1872 ($0.6 F_{TU}$)	1,062	IV	
11	0-1248 ($0.4 F_{TU}$)	8,490	III	
12	0-1248 ($0.4 F_{TU}$)	2,925	IV	
13	0-1248 ($0.4 F_{TU}$)	10,602	III	
14	0-1248 ($0.4 F_{TU}$)	6,500	III & IV	
15	0-1248 ($0.4 F_{TU}$)	5,340	III & IV	
16	0-624 ($0.2 F_{TU}$)	78,000	III	
18	0-624 ($0.2 F_{TU}$)	42,000	III	
19	0-624 ($0.2 F_{TU}$)	82,000	III	
20	0-624 ($0.2 F_{TU}$)	55,000	III	
21	0-624 ($0.2 F_{TU}$)	44,000	III	
22	0-624 ($0.2 F_{TU}$)	60,000	III	

TABLE XXIII. FATIGUE TEST - ADHESIVE WELDBONDED TITANIUM
SPECIMENS - [COMPOSITION APA-BFDA-APA (1 PT);
ALUMINUM (1 PT)] - $F_{TU} = 3,228$ LBS, $R = 0$

Spec. No. J1580-20A	Load Lbs	N Cycles	Failure Mode	Remarks
1	0-2582 ($0.8 F_{TU}$)	82	IV	
2	0-2582 ($0.8 F_{TU}$)	60	II	
3	0-2582 ($0.8 F_{TU}$)	165	II	
4	0-2582 ($0.8 F_{TU}$)	165	II	
5	0-2582 ($0.8 F_{TU}$)	165	IV	
6	0-1937 ($0.6 F_{TU}$)	450	II	Poor Weld
7	0-1937 ($0.6 F_{TU}$)	540	IV	
8	0-1937 ($0.6 F_{TU}$)	720	II & IV	
9	0-1937 ($0.6 F_{TU}$)	510	II	
10	0-1937 ($0.6 F_{TU}$)	585	III & IV	
11	0-1291 ($0.4 F_{TU}$)	4,260	II	
12	0-1291 ($0.4 F_{TU}$)	5,265	II	
13	0-1291 ($0.4 F_{TU}$)	4,590	II	
14	0-1291 ($0.4 F_{TU}$)	3,870	II	
15	0-1291 ($0.4 F_{TU}$)	5,685	II	
16	0-646 ($0.2 F_{TU}$)	29,000	II & III	
17	0-646 ($0.2 F_{TU}$)	59,000	II	
18	0-646 ($0.2 F_{TU}$)	75,000	II	
19	0-646 ($0.2 F_{TU}$)	83,000	II	
20	0-646 ($0.2 F_{TU}$)	64,000	II	

TABLE XXIV. FATIGUE TEST - ADHESIVE WELDBONDED TITANIUM SPECIMENS - COMPOSITION APA-BFDA-APA (1 PT); THERMID 600 (1 PT); ALUMINUM (2 PTS) - $F_{TU} = 1,998$ LBS, $R = 0$ (SERIES J1580-20C)

Spec. No. J1580-20C	Load Lbs	N Cycles	Failure Mode	Remarks
2	0-1598 ($0.8 F_{TU}$)	1,320	II & IV	
3	0-1598 ($0.8 F_{TU}$)	1,890	IV	
4	0-1598 ($0.8 F_{TU}$)	1,290	IV	
5	0-1598 ($0.8 F_{TU}$)	2,670	II & IV	
6	0-1598 ($0.8 F_{TU}$)	960	III & IV	
7	0-1199 ($0.6 F_{TU}$)	6,210	III	
8	0-1199 ($0.6 F_{TU}$)	6,960	III	
9	0-1199 ($0.6 F_{TU}$)	12,360	III & IV	
10	0-1199 ($0.6 F_{TU}$)	6,900	II & III	
11	0-1199 ($0.6 F_{TU}$)	6,885	III & IV	
12	0-799 ($0.4 F_{TU}$)	33,975	III	
13	0-799 ($0.4 F_{TU}$)	36,000	III	
14	0-799 ($0.4 F_{TU}$)	26,000	III	
15	0-799 ($0.4 F_{TU}$)	44,000	III	
16	0-799 ($0.4 F_{TU}$)	32,000	II & III	
17	0-400 ($0.2 F_{TU}$)	331,000	III	
18	0-400 ($0.2 F_{TU}$)	333,000	III	
19	0-400 ($0.2 F_{TU}$)	574,000	III	
20	0-400 ($0.2 F_{TU}$)	107,000	II	
21	0-400 ($0.2 F_{TU}$)	1,761,000	III	

TABLE XXV. FATIGUE TEST - ADHESIVE BONDED TITANIUM
SPECIMENS - COMPOSITION [APA-BFDA-APA (1 PT);
ALUMINUM (1 PT)] $F_{TU} = 798$ $R = 0$

Spec. No. J1580-20D	Load Lbs	N Cycles	Failure Mode	Remarks
2	0-638 ($0.8 F_{TU}$)	30	AD	Adhesive Starved
3	0-638 ($0.8 F_{TU}$)	510	AD	
4	0-638 ($0.8 F_{TU}$)	720	AD	
5	0-638 ($0.8 F_{TU}$)	2,280	AD	
6	0-638 ($0.8 F_{TU}$)	90	AD	
7	0-479 ($0.6 F_{TU}$)	62,000	AD	Resin Starved
8	0-479 ($0.6 F_{TU}$)	135	AD	
9	0-479 ($0.6 F_{TU}$)	42,000	AD	
10	0-479 ($0.6 F_{TU}$)	8,100	AD	
11	0-479 ($0.6 F_{TU}$)	4,500	AD	
13	0-479 ($0.6 F_{TU}$)	2,490	AD	Short Sample Length
14	0-319 ($0.4 F_{TU}$)	168,000	AD	
15	0-319 ($0.4 F_{TU}$)	19,000	AD	
20	0-319 ($0.4 F_{TU}$)	230,000	AD	
18	0-319 ($0.4 F_{TU}$)	9,000	AD	
19	0-160 ($0.2 F_{TU}$)			No failure after 1.7×10^6 cycles

TABLE XXVI. FATIGUE TEST - ADHESIVE BONDED TITANIUM
 SPECIMENS - COMPOSITION: [APA-BFDA-APA (1 PT);
 THERMID 600 (1 PT) ALUMINUM (2 PTS) -
 $F_{TU} = 960 \text{ LBS}$, $R = 0$

Spec. No. J1580-20E	Load Lbs	N Cycles	Failure Mode	Remarks
2	0-768 (0.8 F _{TU})	95	AD	
3	0-768 (0.8 F _{TU})	1,065	AD	
4	0-768 (0.8 F _{TU})	8,100	AD	
5	0-768 (0.8 F _{TU})	630	AD	
6	0-768 (0.8 F _{TU})	540	AD	
7	0-576 (0.6 F _{TU})	4,275	AD	
8	0-576 (0.6 F _{TU})	3,375	AD	
9	0-576 (0.6 F _{TU})	36,000	AD	
10	0-576 (0.6 F _{TU})	960	AD	
12	0-576 (0.6 F _{TU})	43,000	AD	
13	0-384 (0.4 F _{TU})	3,420	AD	
16	0-384 (0.4 F _{TU})	—	No failure after 6 x 10 ⁶ cycles	
19	0-384 (0.4 F _{TU})	147,000		
18	0-384 (0.4 F _{TU})	—	No failure after 2.7 x 10 ⁶ cycles	

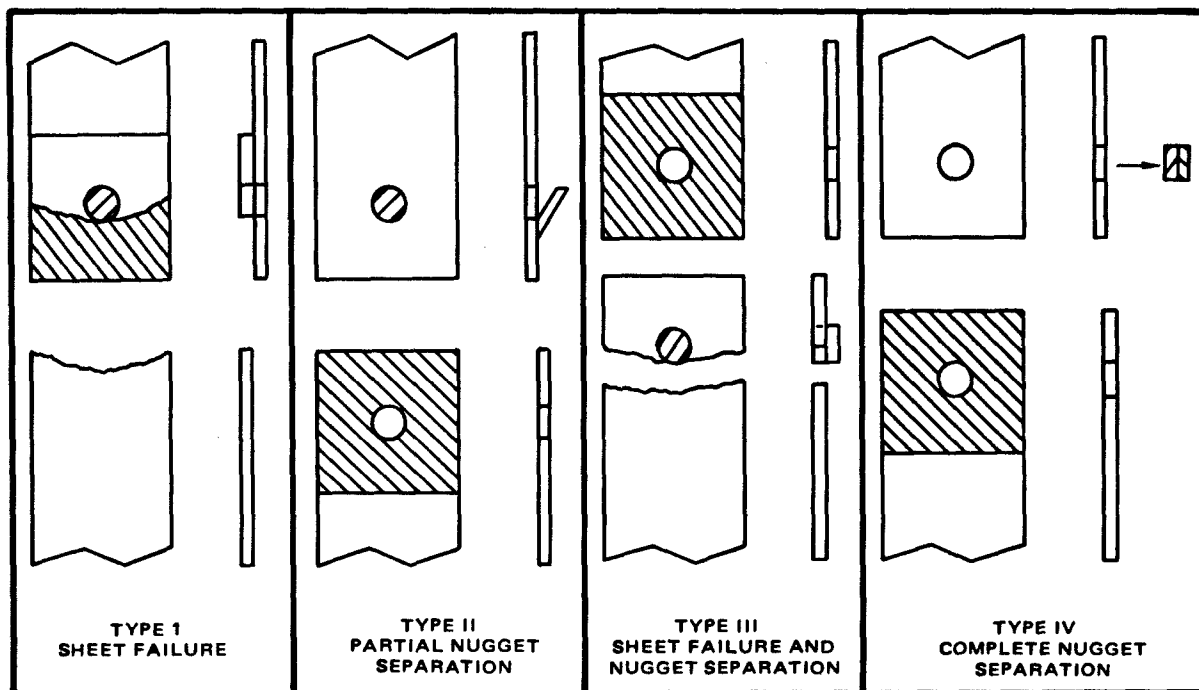


Figure 6. Failure modes observed on weldbonded titanium lap shear fatigue specimens.

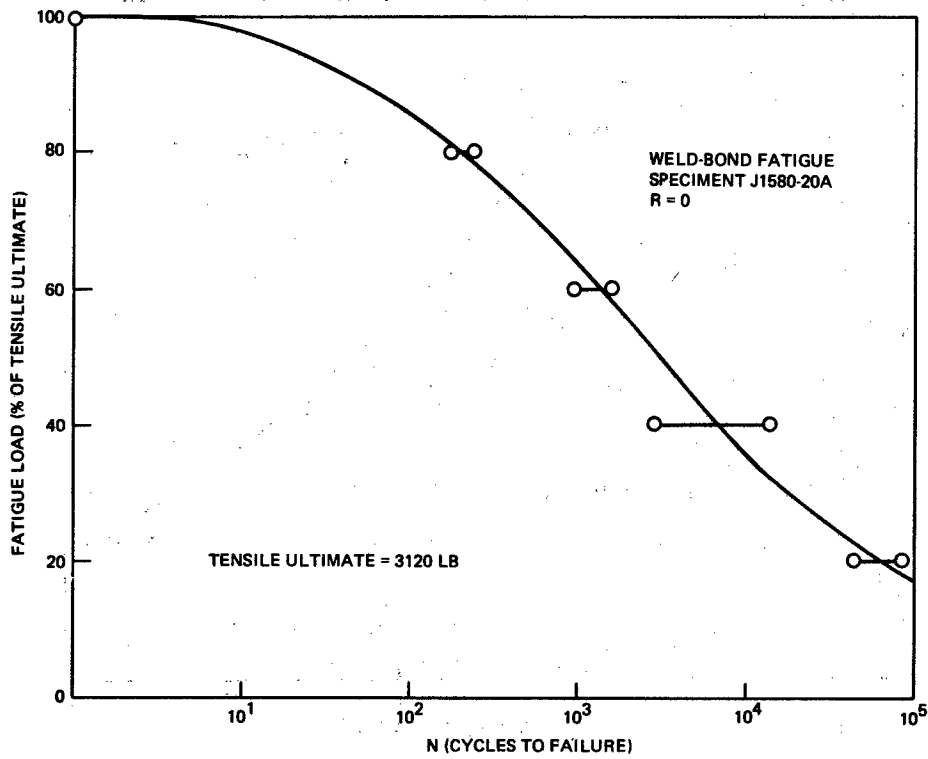


Figure 7. Fatigue test, welded titanium specimens, no adhesive.

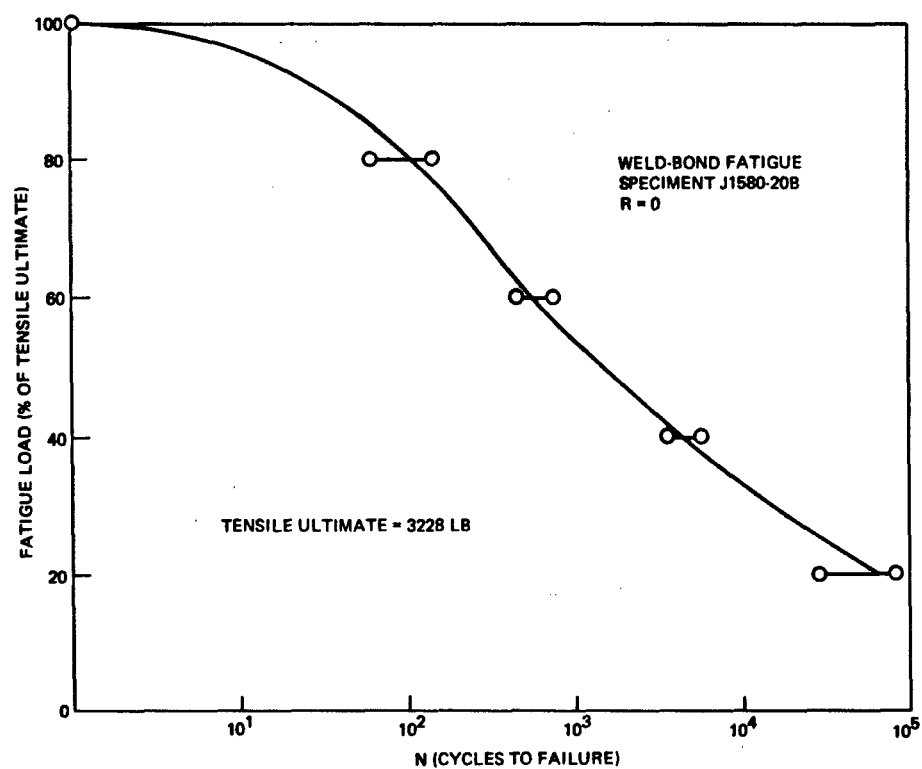


Figure 8. Fatigue test, adhesive weldbonded titanium specimens, composition APA-BFDA-ADA/aluminum.

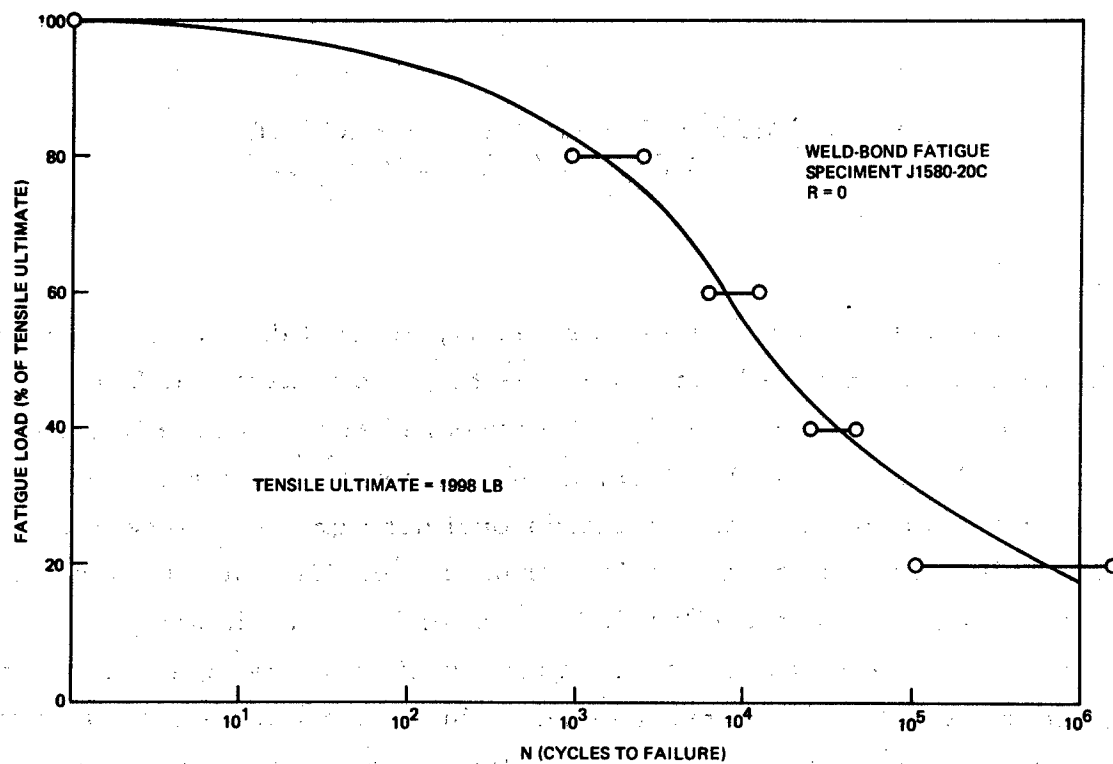


Figure 9. Fatigue test, adhesive weldbonded titanium specimens, composition APA-BFDA-ADA/thermid 600/aluminum.

IV. RECOMMENDED FUTURE DEVELOPMENT OF ADDITION CURED POLYIMIDE RESINS

In the program covered by this report, several diacetylene substituted polyimide monomers have been utilized as reactive diluents for Thermid 600. These materials, which were originally prepared as part of the Hughes Independent Research and Development effort, contain, in the anhydride portion of the prepolymer, a hexafluoroisopropylidene group in place of a carboxyl group. This change in the molecular structure results in a considerably lower melting point (nearly 100°C below that of Thermid) in addition to greatly enhanced solubility in low boiling solvents such as acetone. In addition, mixtures of these diluents with Thermid 600 form homogeneous melt phases with melting temperatures well below the melting temperature of Thermid. The observed high solubility in easily removable solvents coupled with low melting temperatures of reactive diluents and reactive diluent/Thermid mixtures have made it possible to satisfy one of the major objectives of this program — namely that of imparting tack and drape to resin preregs. In addition, the extended liquid range allows for a greater "window" between melt temperature and cure temperature for improved processability over Thermid in preparation of composite structures.

The preliminary reactive diluent work reported here has clearly established the feasibility of the reactive diluent approach to improvement of tack and drape and processability. Continued development of this concept should include the following experimental work:

A. OPTIMIZE COMPOSITION OF REACTIVE DILUENT/THERMID MIXTURES

The majority of the reported diluent study was achieved with a Thermid: Diluent ratio of 2:1. A study should be made to find the most

satisfactory Thermid/diluent ratio. This would involve melting temperature determination and thermal analysis of various mixtures to find the best candidate mixtures. It may be desirable to examine ternary mixtures, i. e., Thermid plus 2 diluents.

B. OPTIMIZE PROCESSING OF CANDIDATE MIXTURES

Glass and graphite prepregs would be made from the more favorable of the Thermid/diluent mixtures by both solvent and hot-melt techniques, preferably by methods suitable to commercial prepegging operations.

C. STUDY THE PREPARATION OF COMPOSITES FROM THE OPTIMIZED THERMID/DILUENT MIXTURES.

Examine autoclave processing to take advantage of the lower resin melting temperatures and lower cure temperatures. Evaluate parameters such as Flex strength, modules, Tg, and long term thermal stability as a function of optimized cure and postcure conditions.

D. EVALUATE NEAT REACTIVE DILUENTS

Evaluate these diluents for use as matrix resins for laminates and molding compounds, and as adhesives for titanium and for composites.

This diluent study should include the four fluorine containing oligomers synthesized previously and utilized in this program as well as cooligomers prepared by using mixtures of "6F" and "BFDA" anhydrides reacted with "BAPB" and "APA" in varying stoichiometric proportions.

V. EXPERIMENTAL

A. PREPARATION OF PREPREGS AND COMPOSITES

1. Materials

a. Fabrics and fibers

- 1) Glass Fabric Type 7781 with a CS-290 finish; Clark-Schwebel Fiber Glass Corp.
- 2) Graphite Fibers
 - a) HTS type, Hercules, Inc.
 - b) Thornel 300, Union Carbide Corp.
- 3) Resins
 - a) Thermid 600, Lot 7D106, Gulf Oil Chem. Co.
 - b) APA-6F-APA Diluent, Lot H2898-46; -57; -76
 - c) APA-6F-BAPB-6F-APA, Lot H2898-25; -45; -59; -63; -79; -80
 - d) APA-BFDA-APA, Lot H2898-55; -91
 - e) APA-BFDA-BAPB-BFDA-APA, Lot H2898-53

2. Process

Glass Cloth Reinforced Composites.

Glass fabric type 7781 with a CS-290 finish was dried at 250°F (121°C) for 2 hours prior to coating. In order to obtain a 45 percent resin pick-up, the Thermid 600 or a mixture of diluent and Thermid 600 was weighed out and dissolved in sufficient N-methylpyrrolidinone (NMP) to give a resin concentration of about 25-35 percent. The fabric was dipped in the hot solution (350°F, 177°C) and oven dried for 5 minutes at 350°F (177°C) between

coats. The fabric was redipped until all the solution was used up. Then the fabric air dried for 45 minutes at 350°F (177°C) prior to molding.

The plies of coated fabric was wrapped in mold release treated aluminum foil and place in preheated press and molded and held at temperature and pressure as indicated elsewhere in text. For the reactive diluents without Thermid 600, acetone was used to prepare the lacquer. A weighed amount of oligomer, calculated to give a 45 percent resin pickup, was dissolved in acetone. The fabric was dipped in the solution at ambient temperature, air dried for 30 minutes between coatings, and redipped until all the lacquer was used up. The fabric was then dried for 1 hour at 160°F (71°C) in an air circulating oven. As before, the prepreg was cut up into the desired dimensions and wrapped with aluminum foil; it was then placed in a preheated press and molded, using the parameters described in the text.

Unidirectional Graphite Fiber Prepregs

Either the Thermid 600 or a mixture with a reactive diluent was weighed out to give a 45 percent resin pickup and dissolved in NMP. A continuous tow was dipped through hot (350°F, 177°C) NMP lacquer solution contained in an impregnator collimator apparatus and wound on a 2-foot diameter drum. The prepreg was removed from the drum and hand collimated to close all gaps between tows. The prepreg was placed on an aluminum plate and dried at 350°F (177°C) for 45 minutes. The prepreg was molded using the parameters described elsewhere in the text.

B. PREPARATION OF ADHESIVE PREPREG AND BONDED TEST SPECIMENS

1. Materials

- a. 112 E Glass Fabric, starch-oil finish, heat-cleaned, source-Clark-Schwebel Fiber Glass Corp.
- b. N-methylpyrrolidinone/benzene imidized HR602, identified as H2350-88A, H2898-21 and H2898-68A.

- c. HR602 prepared as a polyamic acid in N-methylpyrrolidinone and imidized in trifluoroacetic anhydride at room temperature, identified as batches H2350-88B, H2898-22B, and H2898-68B.
- d. HR602 prepared as a polyamic acid in N-methylpyrrolidinone and imidized in refluxing acetic anhydride, identified as batches H2350-95 and H2898-22A.

2. Process

a. Formulation

Mixtures were prepared using prepolymers described above. Ten compositions were used.

- 1) A 50/50 w/w mixture of oligomer H2350-88A and H2350-88B.
- 2) A 50/50 w/w mixture of oligomer H2350-88A and H2350-95.
- 3) Oligomer H2350-88A by itself.
- 4) A 50/50 weight mixture of H2898-21 and H2898-22B containing 25 percent 325 mesh aluminum powder based on resin weight.
- 5) H2898-21 and 10 percent 325 mesh aluminum powder based on resin weight.
- 6) A 50/50 weight mixture of H2898-21 and H2898-22B containing 10 percent 325 mesh aluminum based on resin weight.
- 7) A 50/50 weight mixture of H2898-21 and H2898-22A containing 10 percent 325 mesh aluminum based on resin weight.
- 8) A 50/50 weight mixture of H2898-21 and H2898-22B containing 50 percent 325 mesh aluminum based on resin weight.
- 9) A 50/50 weight mixture of H2898-21 and H2898-22B containing 25 percent 325 mesh aluminum based on resin weight.
- 10) A 50/50 weight mixture of H2898-68A and H2898-68B.

These formulations were dissolved in N-methylpyrrolidinone and used to form a lacquer to prepare the preregs.

b. Prepreg Preparation

An impregnation tank suitable for submerging glass fabric in strip form under the surface of the polyimide solution was heated to about 350°F (178°C). The hot solution of the oligomer in the solvent was added to the preheated tank and the fabric passed through the solution in a continuous impregnation mode. The mixtures containing the aluminum powder were used in slurry form and applied with a brush at room temperature. The drying schedule was used as noted in the text.

c. Lap Shear Specimen Preparation

The titanium specimens were cleaned with a TURCO 5578 alkaline cleaner and etchant for titanium. Thus, the etchant solution was prepared using 900 grams in 2500 ml of water. The following procedure was used.

- 1) Remove organic soils by wiping surface clean with cellulose tissues soaked in toluene or methyl ethyl ketone; or by scrubbing with Ajax (Institutional Grade) or an equivalent abrasive cleaner followed by a rinse with tap, deionized or distilled water to a waterbreak free condition.
- 2) Pickle the specimens for 10 minutes in the alkaline etch solution described above at 180-200°F (82-93°C).
- 3) Rinse with hot water at 180-200°F (82-93°C) for several minutes.
- 4) Rinse with deionized water.
- 5) Dry in air and store in vacuum desiccator until used.
- 6) Cut the prepregs to 1-1/8 inches x 5/8 inch coupons and give them an additional drying time as described in the previous section.
- 7) Place the prepreg between titanium coupons to achieve 1/2-inch lap. To prevent dog-legging, a jig was used and the coupons clamped immediately with spring clamps.
- 8) Use No. 27 spring clips to achieve 15 psi pressure.
- 9) Cure the specimens in the circulating air oven using a cure cycle described in the previous section.

C. PREPARATION OF ACETYLENE TERMINATED POLYIMIDES

1. HR602 Preparation

Experiment H2898-21

A solution of 1, 3-bis (3-aminophenoxy) benzene (52.6 grams, 0.180 mole) in N-methylpyrrolidinone (NMP) (500 ml) was added dropwise to a solution of benzophenonetetracarboxylic dianhydride (BTDA) (86.4 grams, 0.269 mole) in NMP (750 ml) at 55°C over a 1 hour period. After the addition was completed, the solution was stirred for an additional hour. Then a solution of 3-aminophenylacetylene (23 grams, 0.197 mole) in NMP (100 ml) was added all at once. To the solution was added benzene (440 ml) and the solution heated at total reflux under an atmosphere of argon. The

solution was heated a total of 9 hours with the pot temperature at 147°C. A total of 11 ml (theory 8 ml) of water was collected in the trap. The greater than theoretical amount of water collected is due to the water present in the NMP solvent. No attempt was made to dry the NMP prior to use. The solvent was removed on the rotary film evaporator and the residue triturated with absolute ethanol, filtered and triturated three more times with fresh ethanol. The product, when dried at 120°C in vacuum for 6 hours, weighed 142 grams (95 percent of theory) and had a melting point of 175-182°C. It was identified as H2898-21.

Experiment H2898-22

A solution of 1, 3-bis (3-aminophenoxy) benzene (104.5 grams, 0.358 mole) in N-methylpyrrolidinone (NMP) (1000 ml) was added dropwise to a solution of BTDA (172.9 grams, 0.537 mole) in NMP (1500 ml) at 55°C over a 1 hour interval. After the addition was completed, the solution was stirred for an additional hour. Then a solution of 3-aminophenylacetylene (45 grams, 0.385 mole) in NMP (100 ml) was added all at once. The solution was stirred under argon at 45°C for an hour and then divided into two parts.

Part A

The solvent was stripped on a rotary film evaporator. The residue was then heated at reflux for 4 hours with 600 ml of acetic anhydride. The acetic anhydride was then removed using the rotary film evaporator and the residue triturated with absolute ethanol, filtered and triturated three more times with fresh ethanol. The product, when dried at 120°C in vacuum for 4 hours had a melting point of 190-202°C and weighed 123 grams (82 percent of theory). It was identified as H2898-22A.

Part B

The solvent was distilled off on the rotary film evaporator and the residue dispersed in trifluoroacetic anhydride (300 ml) and stirred for several days at room temperature. The trifluoroacetic anhydride was then

distilled off and the residue triturated with absolute ethanol, the slurry filtered and the oligomer triturated two more times with fresh ethanol. After drying for 4 hours at 120°C in vacuum, the product weighed (63 percent of theory) and had a melting point of 170-178°C. It was identified as H2898-22B.

Experiment H2350-88

A solution of 1, 3-bis (3-aminophenoxy) benzene (69.7 grams, 0.239 mole) in N-methylpyrrolidinone (NMP) (500 ml) was added dropwise to a solution of benzophenonetetracarboxylic dianhydride (115.3 grams, 0.358 mole) in NMP (800 ml) at 55°C over a 45 minute interval. After the addition was completed, the solution was stirred for an additional hour. Then a solution of 3-aminophenylacetylene (29.1 grams, 0.249 mole) in NMP (100 ml) was added all at once. The solution was stirred under argon at 45°C for an hour and then divided into two parts, A and B.

Part A

To part A, benzene (300 ml) was added and the solution heated at total reflux using a Dean-Stark trap to collect the water. After heating for 15 hours with a pot temperature of 127°C, a total of 6.0 ml (theoretical 5.4 ml) of water was collected in the trap. The solvent was removed on the rotary film evaporator and the residue triturated with absolute ethanol, filtered and triturated three more times with fresh ethanol. The product, when dried at 120°C in vacuum for 18 hours, weighed 95 grams (95 percent of theory) and had a melting point of 172-176°C. It was identified as H2350-88A.

Part B

The solvent was distilled off on the rotary film evaporator and the residue dispersed in trifluoroacetic anhydride (450 ml) and stirred for 18 hours. The trifluoroacetic anhydride was then distilled off and the residue triturated with fresh ethanol, the slurry filtered and the oligomer triturated two more times in the same manner with fresh ethanol. After drying for 18 hours at 120°C in vacuum, the oligomer weighed 90 grams (90 percent of theory) and melted at 170-175°C. It was identified as H2350-88B.

Experiment H2350-95

A solution of 1,3-bis(3-aminophenoxy) benzene (43.6 grams, 0.149 mole) in NMP (400 ml) was added dropwise to a solution of benzophenone-tetracarboxylic diahydride (70.1 grams, 0.224 mole) in NMP (650 ml) at 45-50°C over a 45 minute period. After the addition was completed, the solution was stirred for an additional hour. Then a solution of 3-aminophenylacetylene (20 grams, 0.171 mole) in NMP (100 ml) was added all at once and stirred for an additional hour. The solvent was stripped on the rotary film evaporator and the residue dispersed in acetic anhydride and heated at reflux for 4 hours.

The acetic anhydride was then removed on the rotary film evaporator and the residue triturated with absolute ethanol. The residue was triturated with fresh ethanol three times in a similar manner and dried for 6 hours at 120°C in the vacuum desiccator. The oligomer weighed 109 grams, (87 percent of theory), had a melting range of 206-214°C, and was identified as H2350-95.

D. PREPARATION OF REACTIVE DILUENTS

1. Reactive Diluent from 3-Aminophenylacetylene (APA) and 2,2-Bis (3,4-Dicarboxyphenyl) Hexafluoropropane Diahydride (6F);
(APA-6F-APA)

Experiment H2898-76

To a solution of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane (6F) (50.0 grams, 0.113 mole) in 30 ml of N-methylpyrrolidinone (NMP), a solution of 3-aminophenylacetylene (27.0 grams, 0.231 mole) in 100 ml of NMP was added all at once. Sufficient benzene was added to give a pot temperature of 149°C at reflux. A Dean-Stark water trap was used to remove the water formed during the imidization. The reaction mixture was refluxed for 13 hours. Then the solvent was removed on the rotary film evaporator. The residue was extracted with petroleum ether and then recrystallized from absolute ethanol. The recrystallized imide melted at 190-194°C, weight 65 grams (90 percent of theory).

Experiment H2898-57

To a solution of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (30.0 grams, 0.0676 mole) in N-methylpyrrolidinone (NMP, 300 ml) kept at 50°C, a solution of 3-aminophenylacetylene (16 grams, 0.137 mole) in NMP (50 ml) was added all at once. Then enough benzene was added to bring the pot temperature to 150°C during total reflux. The mixture was refluxed for 17 hours, the end of which time the pot temperature was 164°C. A total of 4.8 ml (theory, 1.2 ml) of water was collected in the trap. No attempt was made to dry the NMP before use. The solvent was then stripped on the rotary film evaporator and the residue triturated with petroleum ether in the blender.

After filtering, the process was repeated one more time with fresh petroleum ether and twice with absolute ethanol. The product (H2858-57A) was dried overnight in vacuum at 80°C to yield 25.0 grams, m.p. 145-150°C. Another crop of product was obtained from the ethanol wash upon standing overnight. A weight of 4.5 grams (H2898-57B) m.p. 184-186°C was isolated. The filtrate was allowed to stand for several days depositing a third crop of crystals (H2898-57C), 3.5 grams, m.p. 182-185°C. The combined yield, 33.0 grams, was 76 percent of theory. The analyses for H2898-57A was C, 65.31; H, 2.60; N, 4.44, and F, 17.61 percent. The theoretical values for $C_{35}H_{16}O_4F_6N_2$ are C, 65.42; H, 2.49; O, 9.97; N, 4.36; and F, 17.76.

2. Reactive Diluent from 3-Aminophenylacetylene (APA). 2,2-BIS (3,4-Dicarboxyphenyl) Hexafluoropropane Dianhydride (6F) and 1,3-Bis (3-Aminophenoxy) benzene (BAPB) (APA-BAPB-6F-BAPB-APA)

Experiment H2898-59

To a solution of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6F) 44.4 grams, 0.100 mole) in 400 ml of N-methylpyrrolidinone (NMP) at 60-80°C, a solution of 1,3-bis (3-aminophenoxy) benzene (BAPB) (14.6 grams, 0.05 mole) in 100 ml of NMP was added dropwise over a 45 minute period. The mixture was stirred for an additional hour. Then a solution of 3-aminophenylacetylene (12.9 grams, 0.11 mole) in 50 ml of

NMP was added all at once. Sufficient benzene was added to the reaction mixture to give a pot temperature of 148°C during total reflux. The reaction mixture was heated at total reflux for 19 hours during which time 5.0 ml of water was collected in the Dean-Stark trap. The solvent was removed on the rotary film evaporator. The residue was triturated with petroleum ether ($35\text{-}60^{\circ}\text{C}$ boiling range) and then with absolute ethanol using the high speed blender. The oligomer was filtered and the process repeated 3 more times. The washed oligomer when dried at 70°C for 16 hours weighed 64 grams (96 percent of theory) and had a melting point of $155\text{-}160^{\circ}\text{C}$. It was identified as H2898-59.

Experiment H2898-63

To a solution of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6F) (100 grams, 0.2252 mole) in 750 ml of N-methylpyrrolidinone (NMP) at 50°C , a solution of 1, 3-bis (3-aminophenoxy) benzene (BAPB) (32.9 grams, 0.1126 mole) in 250 ml of NMP was added dropwise over a 90 minute period. The solution was stirred for an additional 30 minutes. Then a solution of 3-aminophenylacetylene (APA) (26.4 grams, 0.2252 mole) in 100 ml of NMP was added all at once. Sufficient benzene was added so that the pot temperature was 140°C at reflux. The mixture was heated at total reflux for 19 hours, during which time 12 ml (Theory 8.1 ml) of water was collected in a Dean-Stark trap. No attempt was made to dry the NMP prior to use. The solvent was stripped on the rotary film evaporator. The residue was triturated with absolute ethanol in a blender, filtered and the process repeated three more times with fresh ethanol. The oligomer was dried for 72 hours at 80°C in vacuum. A yield of 134 grams (89 percent of theory) m. p. $147\text{-}152^{\circ}\text{C}$ was obtained.

Experiment H2898-45

To a solution of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (20.0 grams, 0.0451 mole) in N-methylpyrrolidinone (200 ml)

*The analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921.

at 60-70°C, a solution of 1,3-bis (3-aminophenoxy) benzene (6.57 grams, 0.0225 mole) in N-methylpyrrolidinone was added dropwise while maintaining good stirring. Then the solution was stirred for an additional 30 minutes and a solution of 3-aminophenylacetylene (6.0 g., 0.0513 mole) in N-methylpyrrolidinone (50 ml) was added all at once. A Dean-Stark water trap was added to the set-up and enough benzene added to bring the pot temperature to 140°C during reflux. The solution was heated at total reflux for 10 hours during which time 3.0 ml (theoretical 1.6 ml) of water was collected. No attempt was made to dry the NMP prior to use. The solvent was removed on the rotary film evaporator and the residue triturated with cold ether and stirred in the high speed blender. This procedure was repeated three more times. The ether extracts were saved and the oligomer dried in vacuum to yield 18 grams (I. D. No. H2989-45A) having a melting point of 165-175°C. The ether filtrate was concentrated to dryness on the rotary film evaporator. The residue was triturated with petroleum ether in the high speed blender. After vacuum drying at room temperature, a yield of 12 grams, m. p. 50-60°C was obtained (I. D. No. H2989-45B). The low melting point of this fraction was due to the presence of small amounts of NMP. The IR spectra for both fractions were almost the same with the exception that fraction -45B showed the presence of NMP. The combined yields were almost theoretical.

3. Reactive Diluent from 3-Aminophenylacetylene (APA) and 2,2-Bis [4(3,4-dicarboxyphenoxy) phenyl] Hexafluoropropane Dianhydride (BFDA); (APA-BFDA-APA)

Experiment H2898-55

To a solution of BFDA (10.0 grams, 0.0159 mole) in N-methylpyrrolidinone (100 ml, NMP), a solution of 3-aminophenylacetylene (3.72 grams, 0.0318 mole) in NMP (25 ml) was added all at once. Then enough benzene was added to yield a pot temperature of 143°C during total reflux. After heating at reflux for 4 hours, a total of 1 ml (0.6 ml theoretical) of water was collected in the Dean-Stark trap. The solvent was stripped on the rotary film evaporator. The residue was recrystallized from ethanol-water to yield 7.0 grams (53 percent of theory) of product melting at 120-122°C,

I.D. No. H2898-55. This product was very soluble in acetone and had the following analysis*: C, 67.72; H, 3.04; N, 3.46; and F, 12.93 percent. The theoretical values for the expected compound $C_{47}H_{24}O_6N_2F_6$ are C, 68.28; H, 2.91; N, 3.39; and F, 13.80 percent.

Experiment H2898-99

To a solution of BFDA (49.0 grams, 0.0780 mole) in N-methylpyrrolidinone (250 ml, NMP), 3-aminophenylacetylene (18.3 grams, 0.156 mole) was added all at once. Then enough benzene was added to yield a pot temperature of 125°C at total reflux. The reaction mixture was heated at reflux for 5 hours and the water separated with a Dean-Stark type trap. The solvent was stripped on the rotary film evaporator. The residue was recrystallized from ethanol-water to yield 50 grams (77 percent of theory) of product melting at 116-118°C.

Experiment J1580-3

To a solution of BFDA (100.0 grams, 0.159 mole) in N-methylpyrrolidinone (500 ml, NMP), 3-aminophenylacetylene (37.3 grams, 0.3185 mole) was added all at once. Sufficient benzene was added to yield a pot temperature of 145°C. The solution was heated at reflux for 2 hours and the water separated with a Dean-Stark type trap. A total of 420 ml of NMP was stripped on the rotary film evaporator. The syrupy residue was triturated with water and filtered and the product washed with water and hexane. The product was dissolved in benzene and the diimide was precipitated by addition to hexane. A yield of 110 grams (84 percent of theory) m.p. 105-108°C was obtained.

*The analyses were performed by Galbraith Laboratories, Knoxville, TN 37921.

4. Reactive Diluent from 3-Aminophenylacetylene (APA); 1,3-Bis (3-Aminophenoxy) benzene (BAPB) and 2,2-Bis [4(3,4-dicarboxyphenoxy) phenyl] Hexafluoropropane dianhydride (BFDA), (APA-BFDA-BAPB-BFDA-APA).

Experiment H2898-53

To a solution of BFDA (30.0 grams, 0.0476 mole) in N-methylpyrrolidinone (NMP, 250 ml) a solution of 1,3-bis (3-aminophenoxy) benzene (6.95 grams, 0.0238 mole) in NMP (70 ml) was added slowly over a 35 minute period while the temperature was kept at 50-75°C. After the addition the solution was stirred for an additional 30 minutes at 75°C. Then a solution of 3-aminophenylacetylene (6.0 grams, 0.0512 mole) in NMP (50 ml) was added all at once. Sufficient benzene was added so that the pot temperature was 143°C during reflux. The water was collected in a Dean-Stark trap. The mixture was heated at reflux for 9 hours during which time a total of 3.0 ml (theoretical 1.7 ml) was collected. The solvent was removed on the rotary film evaporator and the residue triturated with absolute ethanol using the high speed blender. The product was filtered and triturated three more times with fresh ethanol in the same manner as before. The ethanol washes were combined and concentrated to a total volume of 250 ml. Upon cooling in a dry-ice/acetone bath, more product came out of solution. The product was filtered and triturated with petroleum ether in the high speed blender. The products were combined and dried at 100°C in a vacuum oven. The yield was 32.4 g, (80 percent of theory), m.p. 144-150°C, soluble in acetone (I.D. No. H2898-53). The elemental analysis* for this product showed C, 66.68; H, 2.92; N, 3.45; and F, 14.4 percent. The theoretical values for $C_{96}H_{90}O_{14}F_{12}$ are C, 67.37; H, 2.92; O, 13.10; N, 3.27; and F, 13.33 percent.

*The analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN 37921.

5. Attempted Preparation of N, N' - (Bis-3-ethynylphenyl acetylene)
Dicarboxamide

Experiment H2898-41

In a 500 ml r. b. flask were mixed 3-aminophenylacetylene (35.1 grams, 0.20 mole) and diethyl acetylenedicarboxylate (25.5 grams, 0.30 mole). The mixture immediately started to heat up and it was placed on the rotary film evaporator; vacuum applied and the flask cooled with water. This effectively controlled the exotherm. The water bath was heated to 85°C and the flask rotated for an additional hour. The residue was diluted with about 300 ml of diethylether and the ether solution washed with 5 percent aqueous hydrochloric acid several times to remove unreacted 3-aminophenylacetylene. The residue was allowed to stand overnight whereupon it crystallized. The residue was recrystallized from methanol to yield about 15 grams of a yellow crystalline power, m.p. 60°C having the following analysis: * C, 66.81, 66.65; H, 6.14, 5.96; N, 4.89, 5.07 percent. The theoretical values for the compound $C_{20}H_{12}N_2O_2$ are C, 76.92; H, 3.85; N, 8.97 percent. Based on a molecular weight of 278 ± 10 as determined with the vapor phase osmometer, the elemental analysis gives $C_{16}H_{17}NO_4$ for compound H2989-41.

The compound suggested by this empirical formula is diethyl 2-(3-ethynylanilino) maleate. This compound is the result of the addition of 3-aminophenylacetylene across the acetylenic bond in diethyl acetylenedicarboxylate, namely:



*Elemental analysis by Galbraith Laboratories, Knoxville, TN 37921.